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INORGANIC CHEMISTRY
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INORGANIC CHEMISTRY

FOR

UPPER FORMS

BY

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SENIOR SCIENCE MASTER AT UPPINGHAM SCHOOL



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PREFACE

THIS book is intended for the use of boys in the Upper Forms of schools, and it is assumed that a year's course in Chemistry, both in Practical Work and in Theory, has already been taken. It may, however, be used with advantage by students of maturer years who are beginning the study of Chemistry.

The order of the chapters does not necessarily constitute the order in which the science should be studied—*quot homines, tot sententiae*—the arrangement followed is quite unoriginal.

The Practical Exercises also are not arranged in any definite sequence; they are merely suggested by the bookwork in the chapter to which they are appended. Several of these Exercises are reprinted, with the kind permission of Messrs. Rivington and of my colleague, Major R. P. Shea, from Oscroft and Shea's *Handbook of Practical Chemistry*.

The numerical problems given towards the close of most of the chapters are, many of them, taken from questions set in Cambridge University Scholarship Examinations, and I have to thank the Syndics of the Cambridge University Press for their kind permission to print them; the others are taken from manuscript notes of problems given to my students during a long course of years, and a considerable number of them are, doubtless, taken from various sources

which I am unable to trace. If I have offended anyone in printing them, I apologise most humbly.

My most grateful thanks are due to my colleague, the Rev. J. A. C. Lane, who has read all the proofs for me and has given me most material help with his suggestions, and also to some of my senior students, notably Messrs. W. E. Aylwin, T. E. Hawksley, J. R. B. Kennedy, and B. E. Schlesinger, who read all the manuscript and offered many valuable criticisms.

P. W. O.

UPPINGHAM,

November, 1914.

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CHAPTER I.

INTRODUCTION.

Science. Science is the effort of man towards a universal knowledge of Nature. It is not merely a record of the knowledge gained by observation and experiment, but an effort also to correlate these facts into a system which will define their relation one to another.

Owing to its immensity Science is divided into many branches: Astronomy, Physics, Chemistry, Botany, Zoology, Geology, etc., but, as Francis Bacon says, "The divisions of Science are like the branches of a tree that join in one trunk," and each of them is intimately related to, and, indeed, overlaps others.

Chemistry. The aim of the Science of Chemistry is to classify the knowledge (1) of the different kinds of matter in the universe, (2) of the ultimate constitution of matter, (3) of the phenomena which occur when the different kinds of matter react with one another.

Chemistry is mainly a record of knowledge gained by experiments, but it also attempts to correlate facts thus obtained, to generalize on the results of such experiments, and also often indulges in flights of fancy and theory (short-lived in the main), based on these facts, as to the ultimate composition of matter and of the relations between one kind of matter and another.

Matter has been defined as "anything which occupies space," and, in view of the many different sorts of matter, Chemistry has been subdivided into Inorganic Chemistry, which deals

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with matter which has never been alive, and Organic Chemistry, which deals with matter which has at some time or another been connected with a living organism. At one time a hard and fast line could be drawn between the two divisions, but lately so many Organic substances have been made by purely Inorganic methods—synthetic rubber and synthetic sugar, for instance—that the *raison d'être* for such a division no longer exists.

It is a convenient division to observe, however, and this book will be confined, as far as possible, to the study of Inorganic Chemistry.

Indestructibility of Matter. It must be clearly recognized, at the outset, that there is a limited quantity of matter in the universe; matter can neither be destroyed nor created; it may be changed, different kinds of matter may be compounded or subdivided to form vastly different substances, but the sum total of matter is constant and unvarying.

This is, on the face of it, directly in contradiction of known facts. A wooden match or a piece of paper, for instance, when burnt are destroyed, very little visible matter remaining after the burning, but, as a matter of fact, the solid matter is changed into gaseous matter, which, if collected and weighed, is found to be heavier than the original matter, the extra weight being due to gaseous matter obtained from the air.

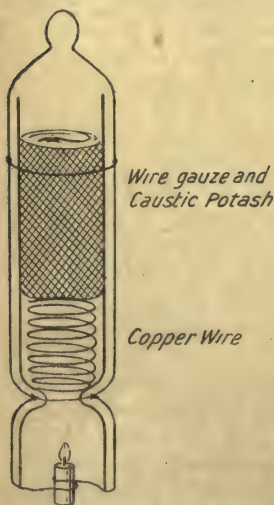


FIG. 1.—Indestructibility of matter.

This is well illustrated by means of the simple apparatus shewn in the diagram (Fig. 1). A candle or night light is burnt under a lamp-glass, the products of the burning, being hot, rise up through the glass. They are first cooled by coming into

contact with a coil of thick Copper wire and then pass through a coil of wire gauze which has previously been dipped into melted Caustic Potash, so that its meshes are filled with solid Caustic Potash. This substance absorbs both the Carbonic acid gas and Steam which are produced by the burning, with the result that the apparatus, if suspended from one arm of a balance, is seen to grow heavier during the combustion, though the wax of the candle is steadily disappearing.

Also, if a clear colourless solution of common Salt is added to a similar solution of Nitrate of Silver, a new kind of matter makes its appearance as a milk white cloud in the liquid, but if the liquids are weighed before, and after mixing, no change in weight will be noticed.

Pure and Impure Substances. The main function of Chemistry being to investigate the properties of different substances, it is clear that it is most necessary for the substance under examination to be perfectly pure, and to contain no extraneous matter of any kind.

The detection of impurities is no simple matter, and a few rules for guidance in this respect are given below.

Solids. A pure solid will shew under the microscope all its grains to be alike in colour, texture and shape; it will have a constant melting point, *i.e.* it will all melt at exactly the same temperature; its action towards various solvents, such as water, acids or alcohol, will be the same all through, *i.e.* it will all dissolve, or none; if part dissolves and part is insoluble, it is impure.

Liquids. The impurities in this case may be either solid, liquid or gaseous. A solid impurity is at once detected by being left behind when the liquid is evaporated. A liquid impurity shews its presence by a gradual rise in the boiling point; the liquid starts boiling at one temperature, which gradually rises as boiling continues; a pure liquid all boils away at the same temperature. A gaseous impurity can nearly always be detected by the fact that it is driven off on boiling the liquid—bubbles of the gas begin to appear on the sides of the vessel in which the liquid is being warmed, and, in nearly every case, the gas is all driven off at the boiling point.

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Gases. Impurities in gases are often very difficult to detect. The solubility or insolubility of an impurity in some solvent, such as water, is of value in some cases, but as all gases dissolve to a small extent in water, this may lead to erroneous deductions. The safest guide is to convert the gas into a liquid and then apply the constant boiling point test; if it all boils away at one temperature, then the original gas must have been pure.

Purification of Substances. Very few pure substances are found in Nature, and, indeed, in manufacture, the early stages result usually in the production of an impure substance sold with the prefix "commercial." Processes of purification must therefore be employed, and a few of those more generally used are given below.

Solids. If the impurity is soluble in water or some other solvent, and the pure substance is not, a thorough washing with the solvent and subsequent drying will leave it pure. If the opposite is the case, the pure substance may be dissolved away in the solvent, and then filtering and evaporation of the clear filtrate will yield the pure substance. If both the substance and its impurity are soluble in water, the process known as "*recrystallization*" may be employed. This depends for its success upon the fact that no two substances are equally dissolved by water, and, if the mixture is completely dissolved in warm water, which is then allowed to cool, the less soluble constituent crystallizes out first, leaving the more soluble in the liquid above it. By a repetition of this process with the crystals formed, a still higher degree of purity is obtained. If neither the substance nor its impurities are soluble, the method of "*liquation*" is sometimes employed; this consists in placing the mixture upon a sloping hearth and heating till the melting point of one of its constituents is reached; this part then flows away down the slope and leaves the rest unmelted.

Liquids. A liquid is freed from solid impurities by "*distillation*." It is turned into vapour, which has none of the solid impurities in it, and, on being cooled again, condenses to a pure liquid. A suitable apparatus for this purpose is shown in the diagram (Fig. 2).

When the impurity is another liquid, the method of "*fractional distillation*" is used. With a similar apparatus to the one used above, the mixture in the flask is heated to boiling. This occurs at the temperature of the boiling point of the most volatile of its constituents, and the temperature gradually rises as boiling proceeds. The distillates are collected in fractions up to different temperatures, and if these fractions are re-distilled, the first portion which distils over contains the most

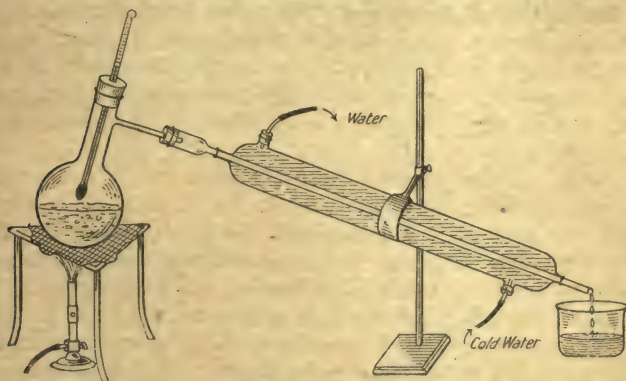


FIG. 2.—Distillation.

volatile part in a high state of purity, whilst the remainder of the last fraction will be the less volatile portion, also very pure.

If the impurity in a liquid is gaseous, it is nearly always expelled by boiling the liquid for a short time.

Gases. Impurities are nearly always removed from gases by causing them to pass through or over some substance which will absorb the impurity, but have no effect upon the rest of the gas. Special absorbents are necessary for each case, and so many cases will be met with in the succeeding pages that it is not necessary to discuss them at this point.

Elements and Compounds. Pure substances are divided by chemists into two classes—Elements and Compounds. An *Element* is a substance which, as far as is known at present, contains one kind of matter only. From it nothing simpler

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has, as yet, been obtained, and, if from it a new substance is made, it is always heavier, never lighter, than the original substance.

About seventy elements are known at the present time; fresh elements are constantly being discovered, and it is quite possible that many of the substances now on the list of elements may soon be found to be complex bodies; hence the reservations in the statements made above.

Elements are usually divided, for purposes of convenience, into *metals* and *non-metals*. It will be found that an exact subdivision is not possible, because some elements exhibit properties characteristic of both classes. The properties of the two classes are contrasted in the following table:

PHYSICAL PROPERTIES.

<i>Metals.</i>	<i>Non-metals.</i>
1. Bright and metallic looking.	1. Dull and without lustre.
2. Specific Gravity high (>4).	2. Specific Gravity low (<4).
3. Malleable and ductile.	3. Brittle.
4. Solids (except Mercury) at ordinary temperatures.	4. Gases, Liquids or Solids at ordinary temperatures.
5. Good conductors of heat and electricity.	5. Bad conductors of heat and electricity.

CHEMICAL PROPERTIES.

6. Oxides are Basic.	6. Oxides are Acidic.
7. Generally dissolve in mineral acids and give off Hydrogen.	7. Do not usually dissolve in mineral acids.
8. Form no compounds with Hydrogen.	8. Form Hydrogen compounds.
9. Form amalgams with Mercury.	9. Form no amalgams.
10. Are liberated at the negative pole during electrolysis.	10. Are liberated at the positive pole during electrolysis.

There are many exceptions to the above, *e.g.* the metals Lithium, Sodium, Potassium, Magnesium and Aluminium have Specific Gravities <4 ; the non-metals Iodine and Graphitic Carbon have a metallic lustre, the latter is also a good conductor of electricity; the metals Bismuth and Zinc are brittle at some temperatures; the metal Palladium forms a definite compound with Hydrogen, etc.

Several elements possess almost equally the properties of

metals and non-metals; to these the name *metalloids* is often given:—the best known are Arsenic and Antimony.

A *Compound* is a substance, pure in itself, but composed of two or more elements united together. It follows, therefore:

- (1) That simpler kinds of matter can be obtained from it.
- (2) That it can be built up from simpler kinds of matter.
- (3) That it can be changed into different substances which weigh less than the original amount taken.

Complex substances, that is, substances which contain more than one kind of matter, are not necessarily compounds, as the two (or more) kinds of matter may not be united together, but only mixed without combination.

Such a substance is termed a *Mixture*, and it is highly important to be able to distinguish between the two classes, Compounds and Mixtures.

The chief points of difference are summarized in the table given below:

Compound.

1. The proportions in which the parts are present are fixed and invariable in the same compound.
2. Its properties are entirely different from those of its parts.
3. It cannot be separated into its parts by mechanical methods or by solution.
4. It has a fixed Melting point and Boiling point.
5. The combination of the parts is usually accompanied by evolution of heat.

Mixture.

1. The proportions in which the parts are present may vary indefinitely.
2. It possesses the properties of its parts. (Of course, these may often oppose or modify one another.)
3. It can be separated into its parts by mechanical methods or by solution.
4. Its Melting point and Boiling point vary.
5. No heat is evolved when the parts are mixed together.

As an example, to illustrate these points of difference, a mixture of powdered Iron and Flowers of Sulphur may be taken.

- (1) They may be mixed in any proportion whatever.
- (2) The mixture possesses the properties both of Iron and Sulphur. For instance, if a little of it is placed in the flame, it gives forth bright sparks as Iron does, and also burns with

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a blue flame as does Sulphur ; its colour is a mean between that of Iron and of Sulphur ; if placed in dilute Hydrochloric acid, Hydrogen gas is evolved just as with Iron, the Sulphur being unaffected.

(3) It can be separated into Iron and Sulphur by means of a magnet, which attracts the Iron and leaves the Sulphur, or by shaking it up with water, when the heavier Iron sinks at once and the lighter Sulphur can be poured off with the water ; these are purely mechanical methods.

Also the Iron can be dissolved away by Hydrochloric acid and the Sulphur left, or the Sulphur, by means of Carbon Disulphide, leaving the Iron unaffected.

(4) When warmed the Sulphur melts at 118° C., leaving the Iron still solid.

(5) If a thermometer is placed in the mixture when it is being made, no rise of temperature is noticed.

If some of this mixture is placed in a test tube and heated till the Sulphur begins to boil, combination takes place between the Iron and the Sulphur, the mass grows red-hot with the heat evolved (exemplifying point No. 5 in the table), and eventually a compound called Ferrous Sulphide is left behind.

(1) If a certain known weight of Iron (7 grams say) is taken for this experiment and excess of Sulphur added, it will only take up a fixed weight of Sulphur (4 grams), and any excess will be left over and may be boiled away. Its proportions therefore are fixed and definite.

(2) Its properties are quite different from those of Iron and Sulphur. In colour it is darker even than Iron, no part of it is attracted by a magnet, it glows dully red when placed in the flame, and with Hydrochloric acid the foul-smelling gas Sulphuretted Hydrogen is evolved.

(3) The parts cannot be separated by a magnet, or by shaking in water, and no solvent will take away one part and leave the other.

(4) It has a perfectly definite melting point, and all of it melts at the same temperature.

(5) Has already been discussed.

PRACTICAL EXERCISES.

To obtain a pure specimen of Sand from Sea-Sand or Sandstone. The impurities present in sea-sand are principally Salt, Calcium Carbonate from broken shells, and Ferric Oxide covering the grains of Sand, whilst in Sandstone the chief impurity is Ferric Oxide, which acts as a cement to the grains. All these impurities are soluble in dilute Hydrochloric acid, which does not affect the pure Silica itself. To purify the Sea-Sand or Sandstone, therefore, digest about 10 grams of it with warmed dilute Hydrochloric acid in a beaker for some time, pour off the acid and add distilled water; repeat the process, adding more distilled water, and then filter. Dry the Sand on the filter paper in a cone over a sand bath (Fig. 3), and the specimen of Sand obtained should be pure.

Test its purity by shaking a little of it up with distilled water and adding a solution of Silver Nitrate; this should give no milkiness if all the impurities have been dissolved out and washed away.

To obtain Pure Potassic Chlorate from a specimen contaminated with Potassic

Chloride. Both the Chlorate and Chloride of Potash are soluble in water—in hot water their solubilities are equal, but, in cold water, the Chloride is much more soluble than the Chlorate. They may therefore be separated by fractional crystallization.

Take about 15 grams of the mixture in a boiling tube, and fill two-thirds of the tube with distilled water. Boil till all is dissolved, and allow to cool. The crystals formed will sink to the bottom of the test tube. Pour off the clear liquid, add distilled water till the tube is half full, and repeat the process of heating and cooling. Pour off the liquid as before, and shake

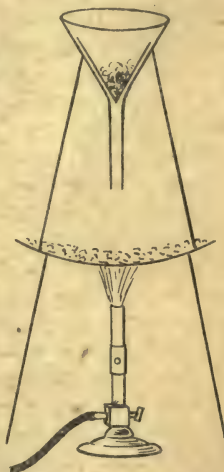


FIG. 3.—Drying in a filter funnel on a cone.

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up the remaining crystals with one-third of a test tube full of cold distilled water. Pour away the water, and the remaining crystals should be pure Potassic Chlorate.

Test their purity by dissolving a little in distilled water and adding a solution of Silver Nitrate, which should produce no turbidity, shewing that all the Chloride has disappeared.

To obtain a specimen of pure Salt from a Mixture of Salt and Alum. In cold water both these substances are about equally soluble, but in boiling water Alum is much more soluble than Salt.

To separate the mixture, take about 20 grams of it in a porcelain dish and add 50 c.c. of distilled water, boil till about 20 c.c. of the liquid is left, allow the Salt to subside and pour off the liquid from it. Repeat the process with the residue and a smaller quantity of distilled water. Wash the resultant solid with a few c.c. of boiling water, and the remaining solid, when dried on filter paper, should be pure Salt.

Test its purity by dissolving a little in distilled water and adding a solution of Barium Chloride. This should give no turbidity, if all the Alum has been taken away.

CHAPTER II.

THE ATMOSPHERE.

THE Atmosphere is the name given to the gaseous envelope which surrounds the earth, which is commonly called the Air. Up to the beginning of the nineteenth century, the term Air was used for all gaseous substances, with various prefixes shewing the nature of the gas, *e.g.* "inflammable air" for the gas Hydrogen, "dephlogisticated air" for Nitrogen, "fixed air" for Carbonic Acid gas, etc.

The Gases of the Air. Air is found to contain many gases, but the two principal ingredients are Oxygen and Nitrogen.

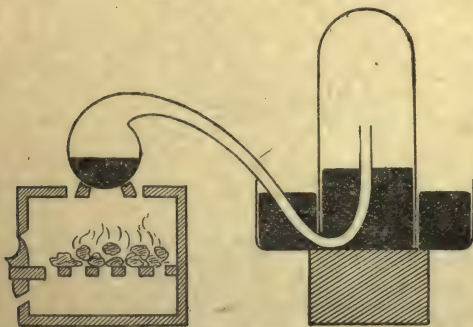


FIG. 4.—Lavoisier's experiment.

The presence of these two gases in air was first definitely proved by the eminent French chemist Lavoisier, in 1775. His experiment, which was of the supremest importance,

consisted, firstly, in the heating of Mercury, for several days, at the temperature of its boiling point, in a glass flask with a long curved neck (Fig. 4), the open end of the neck being in a vessel of air, placed in a basin of Mercury. He noticed that, after a time, a red scum was formed on the surface of the Mercury in the flask, and, at the same time, the volume of the air in the glass vessel was diminished to about four-fifths of its original amount—clearly the Mercury had absorbed some of the air.

On testing this air remaining in the vessel, Lavoisier found that it would not support life, or combustion, so that it was clearly very different from ordinary air. For these reasons it was called Azote, a name he afterwards changed to that of Nitrogen.

Lavoisier next proceeded to take some of the red scum, called at that time Calx* of Mercury, and heat it strongly in a glass tube. A gas was evolved which rekindled a glowing splinter of wood, and Mercury was left behind in the tube; to this gas, later, he gave the name of Oxygen.

Finally, Lavoisier mixed the Oxygen evolved from the Calx with the Nitrogen remaining in the glass vessel, and found the resulting mixture had all the properties of ordinary air and would readily support life and combustion. By these experiments he proved, quite conclusively, the presence of the two gases Oxygen and Nitrogen in air.

The Composition of Air by Volume. In order to determine, with fair accuracy, the percentage of Oxygen present, by volume, in air, a very simple apparatus, due to Hempel, is used (Fig. 5).

The graduated tube *A* is first filled with water and then a measured quantity of air is drawn in, by lowering the tube *B*, care being taken that the levels of water in the two tubes are the same when the reading is taken; the stop-cock is then closed. The tube *A* is then connected to the rest of the apparatus by a short piece of pressure tubing *C*, and, by

* Calx was the name given to all earthy substances produced when metals were heated or burnt in air, *e.g.* Calx of Lead, now called Litharge, Calx of Zinc, now Zinc Oxide.

raising the tube *B* and opening the stop-cock, the air is forced into the bulb *D* containing lumps of Phosphorus in water, the latter being driven into the bulb *E*. When all the air is driven out of the tube *A*, the stop-cock is closed and the Phosphorus gradually absorbs the Oxygen, forming white fumes of Oxides

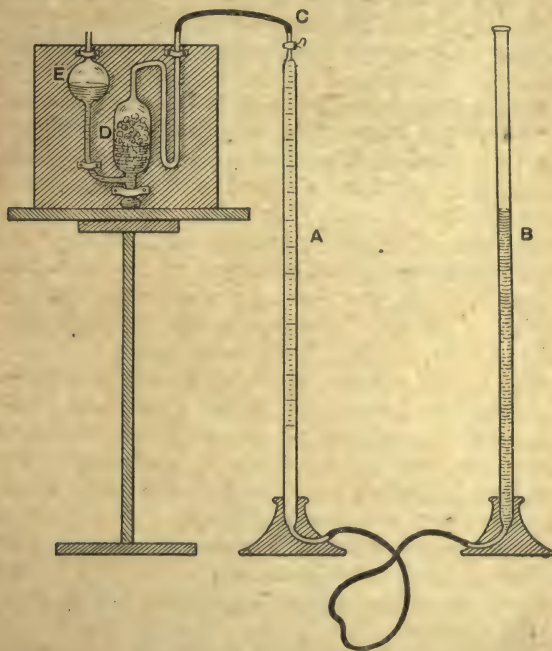


FIG. 5.—Composition of air by volume.

of Phosphorus, which dissolve in the water. As soon as the gas in the bulb *D* is quite clear, it is drawn back into *A*, by opening the stop-cock and lowering the tube *B*; the water-levels are made equal and its volume is measured, the loss of volume being due to the Oxygen absorbed.

By this apparatus values, which approximate very closely to 20.9 per cent. of Oxygen, can be obtained.

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In the latest and most accurate form of this apparatus, due to Jolly, the Oxygen is absorbed by a spiral of Copper wire, heated to redness by an electric current, and the volume of Oxygen calculated from the diminution of pressure in a Mercury pressure gauge, to which the globe containing the Copper wire and the air is attached.

Samples of air collected from all parts of the world and from all altitudes, when analysed, shew a variation in the volume of Oxygen present from 20.86 to 20.99 per cent.

The Composition of Air by Weight. A method by which the proportions of Oxygen and Nitrogen present, by weight, in air can be determined, is that first employed by Dumas and Boussingault.

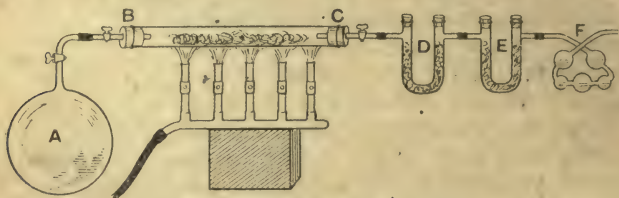


FIG. 6.—Composition of air by weight.

It consists in passing purified air over heated Copper to absorb the Oxygen, collecting and weighing the Nitrogen, and noting the increase in the weight of the Copper (Fig. 6).

The glass globe *A* is exhausted of air, as far as possible, by means of an air pump and then weighed; it is connected to a glass tube *BC*, previously weighed, containing Copper turnings heated to redness in a furnace; this is, in turn, connected to two U-tubes *D* and *E*, containing pumice stone soaked in strong Sulphuric acid, to absorb the water vapour in the air, and a set of Liebig's Potash bulbs *F*, to absorb the Carbonic acid gas in the air.

As soon as the Copper becomes red hot, the stop-cocks are cautiously opened, and air is allowed to be drawn very slowly through the apparatus; when no more air is drawn in, the stop-cocks are closed and, when cool, the tube *BC* and the

bulb *A* are weighed. The increases give the weights of Oxygen and Nitrogen present respectively, and from them the percentages can be calculated. Accurate analyses give 23 per cent. of Oxygen by weight.

Air a Mixture, not a Compound. Neglecting, for a moment, the small quantity of other gases present in the air—they will be discussed later—the question now arises : Is air a mixture or a compound of Oxygen and Nitrogen ? By referring back to the table of differences between mixtures and compounds (p. 7), and applying the tests there enumerated to air, it is found :

(1) The proportions of Oxygen to Nitrogen present in air do vary very slightly, though the variation is a very small one.

(2) The properties of air are not quite different from those of Oxygen and Nitrogen ; *e.g.* Oxygen, Nitrogen and Air are all colourless, odourless gases, which dissolve very sparingly in water ; the density of air (14.4 when Hydrogen=1) is that to be expected from a mixture of 79 parts of Nitrogen (density=14), and 21 parts of Oxygen (density=16) ; Oxygen is an excellent supporter of combustion, Nitrogen is a non-supporter of combustion ; Air is the happy mean and supports combustion fairly well, etc.

Compounds of Oxygen and Nitrogen are known which possess colours and odours, are soluble in water, and whose densities are much greater than would be expected from their composition if the gases were mixed.

(3) The partial separation of the Oxygen and Nitrogen in air can be brought about by purely mechanical means and by solution. They are separated mechanically owing to the different rates at which the two gases diffuse through a porous septum (p. 65). If the round-bottomed flask *D* (Fig. 7) is exhausted as far as possible of air, through the tap *A*, by means of an air-pump, and then by opening the tap *B*, *A* being

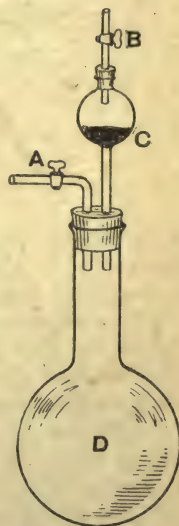


FIG. 7.—Separation of air by diffusion.

shut, air is allowed to diffuse through a porous plug *C*, made of Plaster of Paris, into the flask, this diffused air is found, on subsequent analysis, to contain more than 80 per cent. of Nitrogen. Again, if the small quantity of air, which is found dissolved in water, is expelled by boiling, and analysed, it is found to contain more than 30 per cent. of Oxygen. These changes of composition would not take place if air was a compound of Oxygen and Nitrogen.

(4) If liquid air (p. 179) is allowed to boil away slowly, it is found to commence boiling at a temperature of -194°C. , when most of the Nitrogen is evolved, but the boiling point gradually rises to a temperature of -184°C. , when the Oxygen all boils away.

(5) If 79 parts, by volume, of Nitrogen gas are mixed with 21 parts, by volume, of Oxygen gas, the mixture behaves in every respect like ordinary air, and, at the same time, no signs of chemical action are seen, such as evolution of heat or contraction in volume, whilst the mixture is being made.

On all these five counts, therefore, it is clearly seen that air must be a mixture and not a compound of Oxygen and Nitrogen.

Other Gases in Air. *Water Vapour.* If a small quantity of anhydrous Copper Sulphate is left exposed to the air for a short time, it gradually turns blue; water is the only substance which brings about this change, and water vapour is always present in the air, but in very varying amounts. The quantity present at any particular time can be ascertained by drawing a known large quantity of air

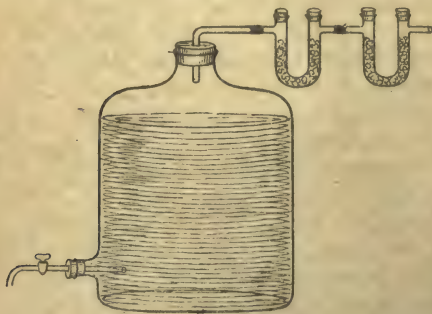


FIG. 8.—Estimation of water vapour in air.

(about 50 litres) by means of an aspirator (Fig. 8) through two U-tubes filled with small fragments of Calcium Chloride;

this substance absorbs the water, and the increase in weight of the U-tubes gives the weight of water vapour in the quantity of air which has been drawn through the apparatus.

One cubic metre of air, when saturated with water vapour, contains at 0° C. 4.87 grams, at 10° C. 9.36 grams, at 30° C. 30.09 grams of water, so that the quantity of water present in air may be said to vary between these limits.

Carbon Dioxide. Lime water, if exposed to air, rapidly acquires a white coating, and eventually forms a white deposit of Chalk, due to the Carbon Dioxide gas which is always present in air.

The processes of breathing, combustion, putrefaction and decay are all attended by the evolution of Carbon Dioxide gas, hence it is usually present in larger quantities in the air of towns and in ill-ventilated rooms than in ordinary air.

The quantity of this gas present in normal air is about 3 parts per 10,000 of air. Strangely enough, the air on some high mountain peaks has been found by Frankland to contain more than the normal amount of Carbon Dioxide; this is thought to be due to the absence of vegetation in these high altitudes.

The quantity of Carbon Dioxide present in any specimen of air is best determined by shaking 3 or 4 litres of the air in a large flask with a known quantity of a dilute solution of Barium Hydrate of known strength; this substance absorbs all the Carbon Dioxide, forming Barium Carbonate, which may either be filtered, dried and weighed, or the quantity of Barium Hydrate, which is left over unchanged by the Carbon Dioxide, may be determined by neutralization with a standard solution of Hydrochloric Acid, p. 50.

Ammonia. When nitrogenous organic matter decomposes, this gas is often evolved and finds its way into the air; it is, for this reason, most often present in the air of towns. The amount present varies considerably, it is always most difficult to detect at all, and, owing to its great solubility in water, Ammonia is practically non-existent after a shower of rain.

Nitric Acid. Whenever the electric discharge known as a flash of lightning occurs in air, Nitric acid is always produced

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Since it is soluble in water, traces of it are nearly always to be found in the rain which falls during or after a thunder-storm.

Ozone. An electric discharge through air is also capable of turning some of the Oxygen in the air into Ozone, and the presence of this gas can often be detected in country or sea air by exposing strips of iodized starch paper for some time to it, when they are turned blue by the Ozone. Owing to its active oxidizing powers, it is never detected in the air of towns or houses, as it would be at once decomposed by any decaying matter present.

Hydrogen. Dewar, in the year 1900, discovered that the first and most volatile portions of gas, which distil off from liquid air, are quite rich in Hydrogen gas. Its average amount has been calculated by Gautier to be 2 parts in 10,000 of air. Its presence is most probably due to the evolution of it from volcanic vents and petroleum springs.

Argon, etc. Rayleigh and Ramsay, in the year 1894, discovered, amongst the Nitrogen of the air, a still more inert gas to which the name Argon was given. Later, Ramsay discovered, amongst the Argon, four more gases, called Helium, Neon, Zenon and Krypton; all five are, as far as is at present known, quite unimportant in their action.

The average composition of Normal Air is, in parts per 1000:

Nitrogen	-	-	769.50
Oxygen	-	-	206.59
Water	-	-	14.00
Argon, etc.	-	-	9.37
Carbon Dioxide	-	-	0.34
Hydrogen	-	-	0.19
Ammonia	-	-	0.01
Ozone	-	-	trace
Nitric Acid	-	-	trace

1000.00

The Rusting of Iron in Air. When a strip of clean Iron or Steel is left exposed to the air for some time, a dark red coating

is formed on it which is usually called rust, and consists chemically of Hydrated Ferric Oxide.

If the strip is weighed before and after rusting, it is found to have gained a little in weight, and therefore the Iron must have taken something from the air in order to form the rust.

Rust is found to form more readily where drops of water are sprinkled upon the Iron, and Iron nails rust readily even when immersed fully under water. It appears, then, as if the water vapour in the air is alone responsible for this change.

This may readily be disproved by placing some clean nails in a round-bottomed flask, adding sufficient water to cover them well, boiling the water vigorously, for some minutes, till the steam has driven all the air out of the flask, and corking it up at once to prevent further ingress of air. Nails, under such conditions, may be kept for years without shewing a trace of rust.

This experiment clearly proves that both water and air are necessary in order that iron may rust.

The following experiment throws considerable light upon the phenomenon of rusting.

Place a few clean iron nails at the bottom of a deep gas jar (Fig. 9), fill up about two-thirds of the jar with well boiled water, slide down to the surface of the water two circular bungs, with most of their central portions cut out, which fit the jar tightly, and which hold between them a circular disc of white blotting paper; then fill up to the top of the jar with well boiled water; this latter will have to be replenished as it evaporates, and the level of the water must never get as low as the blotting paper. After some weeks, rust is observed to form on the surface of the filter paper only, the nails themselves being quite free from it.

From this experiment it is clear that particles of Iron pass, in some way, into solution in the water, rise through the filter paper, and form rust at the surface of the water only, where they come into contact with the Oxygen of the air; and then



FIG. 9.—The rusting of Iron in Air.

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the rust, being insoluble in water, separates out and, as it sinks towards the bottom of the jar, is intercepted by the blotting paper.

To corroborate this experiment, it will be noticed that, if some nails are placed at the bottom of a jar containing water, which is kept still for some time, rust only forms on the parts of the nails which face upwards—never at the sides or under-part—and on the bottom of the jar.

Action of Animals and Plants on Air. If two flasks, each containing one or two inches of Lime water at the bottom,

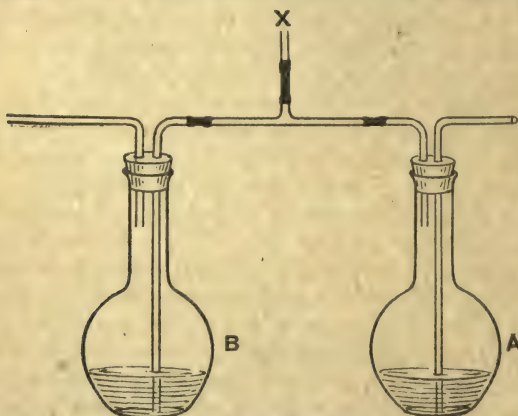


FIG. 10.—The effect of breathing upon the Carbonic acid gas in Air.

are arranged (Fig. 10) so that, by applying the mouth to the tube X, air may be inhaled through the Lime water in the flask A, and exhaled through that in B, it is found that, very shortly, the Lime water in B becomes milky, while that in A is still quite clear.

This indicates an excess of Carbon Dioxide in exhaled air as compared with ordinary air, and the exhaled air will also be found, on analysis, to contain less than 20 per cent. of Oxygen.

Again, if a candle or match is burnt in an enclosed jar of air, it very soon goes out, leaving practically no trace of Oxygen in the jar, and the residual gas is found to contain a

large percentage of Carbon Dioxide. This gas is also found at the bottom of old wells which contain decaying vegetable matter ; its presence may be detected there by lowering into the well a lighted candle, which is very promptly extinguished.

It is thus seen that breathing animals and burning or decaying matter all take Oxygen out of the air, replacing it partly or wholly by Carbon Dioxide, and clearly, if there were no counterbalancing action taking place, the earth would soon become uninhabitable owing to loss of Oxygen.

This counterbalancing action is supplied by the green parts of growing plants, which contain a substance, Chlorophyll, which possesses the property, in sunlight or diffused sunlight, of splitting up the Carbon Dioxide, retaining the Carbon to build up plant tissues and ejecting the Oxygen.

The "stiffness" of ill-ventilated rooms, in which people have been breathing or gases and lamps have been burning for some time, and the bad effect of such an atmosphere on the health of the human body, was long thought to be due to the decrease in the amount of Oxygen and increase in the amount of Carbon Dioxide only. It is now known that this is not entirely the cause of the trouble, but a great deal of it is brought about by the poisonous effects of organic matter evolved during respiration, as indeed this is also the origin of the unpleasant smell experienced on entering such a room.

When the air from a vitiated atmosphere is allowed to play on the cold surface of a mirror, the moisture in it is condensed, and, if preserved for some time, the water rapidly becomes putrescent, owing to the decomposition of the organic matter present in it, aided by the bacteria which it also contains, or which may already be present in untainted air.

The bacteria which produce fermentation, putrefaction and disease are always present in air ; this fact can be demonstrated by carefully keeping milk, flesh or a solution of grape sugar, from all suspended matter by means of a cotton wool plug in the neck of the vessel containing them, when it will be found that no souring of the milk, putrefaction of the flesh or fermentation of the sugar takes place for a very great length of time

PROBLEM.

1. 85.3 c.c. of a gaseous mixture containing Nitrogen, Oxygen and Carbon Dioxide became 83.65 c.c. after treatment with Caustic Potash, and a further contraction to 73.5 c.c. occurred after being treated with Pyrogallic acid and Potash. Find the percentage composition of the mixture.

PRACTICAL EXERCISES.

To find the percentage of Nitrogen in Air. Use a tube about 70 cm. long and 1 cm. internal diameter, closed at one end.



FIG. 11.—Percentage of Nitrogen in Air.

Fill about 10 cm. of the tube with a solution of Pyrogallic acid. Place the tube in a nearly horizontal position, and put a small piece of solid Caustic Potash in the open end and cork it *at once* with a rubber cork. Allow the Potash to mix with the Pyrogallic acid, and shake the tube vigorously for 15 minutes. The acid should then have absorbed all the Oxygen in the tube. Allow the tube to rest in a vertical position, and mark the position (*B*, Fig. 11) of the surface of the Pyrogallic acid. Then measure the distance *AB*, which is a measure of the Air originally in the tube. Next, uncork the tube in a deep vessel of water, and mark the level *C* to which the liquid rises when the levels inside and outside the tube are the same. Measure *AC*, which gives the volume of the remaining Nitrogen gas.

Calculate the percentage which *AC* is of *AB*, which gives the percentage of Nitrogen in Air.

The Rusting of Iron in Air. Set up an apparatus, as described on p. 19 and illustrated in

Fig. 9. The rusting effect will not be observed for several days, but the experiment may extend over a long interval of time, if the water is replenished as it evaporates and is not allowed to get below the level of the blotting paper.

To find the Weight of a Litre of Air. Use a round-bottomed flask of about 300 c.c. capacity, fitted with a rubber cork, having one hole bored in it, through which passes a short

piece of glass tubing. Fit a short piece of rubber tubing on to the glass tube, and have a piece of glass rod handy to close the rubber tube. Place about 25 c.c. of water in the flask and boil for 3 minutes, till the steam has driven out all the Air from the flask. Quickly close the rubber tube with the glass rod and, when quite cool, weigh accurately.

Then admit Air by taking out the glass rod, and weigh again. The increase in weight is the weight of the admitted Air.

Find its volume by first measuring the water left in the flask and then filling the flask completely with water and measuring this water. The difference between these volumes is the volume of Air which entered the flask, and as its weight is known, the weight of one litre of Air can be readily calculated.

A good result should be near 1.29 grams.

CHAPTER III.

OXYGEN.

Symbol, O. Atomic Weight, 16. Molecular Weight, 32.

History. The discovery of Oxygen is usually attributed to the Swedish chemist Scheele, sometime before 1773. He made it by heating (1) the red Oxide of Mercury, (2) a mixture of Sulphuric acid and Manganese Dioxide, and (3) Saltpetre, but did not publish the account of his work till 1777. Meanwhile Priestley, of Birmingham, discovered it quite independently in 1774, by heating the red Oxide of Mercury by means of the sun's rays, concentrated by a large burning glass or lens. It is quite possible from indications in old books that the Greeks knew of Oxygen in the fourth century, and the Chinese even before that time.

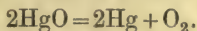
Occurrence. Oxygen is by far the most abundant element on the earth's surface. Air contains 23 per cent. of it, water nearly 89 per cent., and the solid crust of the earth about 47 per cent.

Preparation. (1) The experiments of Priestley and Scheele may be reproduced with a more modern form of the apparatus (Fig. 12), Mercuric Oxide being placed in the tube *A*, connected by the tube *C* to a Mercury gas trough; by this means a small quantity of very pure Oxygen can be collected in the tube *D*, if the first two or three tubes which are filled are discarded.

The Mercuric Oxide, on heating, darkens in colour and begins to evolve Oxygen; Mercury vapour is also given off, and this condenses in the bend *B*. By this experiment it is

seen that Mercuric Oxide when heated splits up into the two elements Mercury and Oxygen.

This is conveniently expressed in the form of what is known as a chemical equation, thus :



Chemical equations represent not only the substances present at the beginning (on the left side) and the end (on the right side) of a chemical action, but also the proportions in

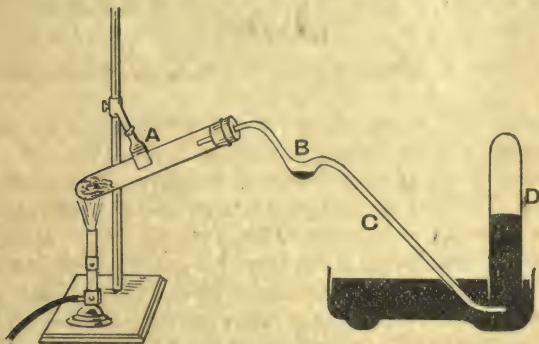


FIG. 12.—Preparation of Oxygen from Mercuric Oxide.

which the various substances take part in the reaction. These proportions are given by the Molecular Weights of these substances taken in the indicated proportions.

For example, repeating the above equation,

$$\begin{aligned} 2\text{HgO} &= 2\text{Hg} + \text{O}_2, \\ 2(200 + 16) &= 2(200) + 2(16), \\ 432 &= 400 + 32. \end{aligned}$$

Hence we can certify that 432 parts of Mercuric Oxide, if completely decomposed, yield 400 parts of Mercury and 32 parts of Oxygen.

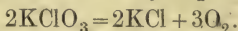
(2) For experimental purposes Oxygen is best obtained from Potassium Chlorate. This solid, on heating, melts at 340°C . ; at 350°C . it appears to boil, and gives off Oxygen ; presently the bubbling ceases and the mass thickens and solidifies ; it is

now a mixture of Potassium Perchlorate and Potassium Chloride. This reaction is represented by the equation



On further heating to 600°C . the Perchlorate splits up, gives off its Oxygen, and the ultimate solid left in the tube is Potassium Chloride.

The result arrived at is usually expressed by the equation



Velocity of Reaction. The influence of rise of temperature upon a chemical process is well exemplified in this experiment, in which, clearly, the higher the temperature, the more rapid the evolution of the Oxygen.

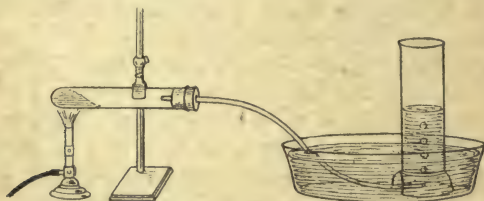


FIG. 13.—Preparation of Oxygen from Potassic Chlorate.

This is a general rule in all chemical reactions, viz. the velocity of the reaction, as it is called, increases with the temperature. The rate of increase is that it doubles, approximately, for every 10°C . rise in temperature, so that a rise of 100°C . would increase the velocity 1024 times, while one of 200°C . would increase it over a million times.

It is possible, then, that Potassic Chlorate is giving off Oxygen at the ordinary temperature of the air, but the velocity of the reaction is so small that the change is quite inappreciable.

When Potassium Chlorate is mixed with $\frac{1}{4}$ of its weight of Manganese Dioxide and warmed, the Oxygen is expelled at a lower temperature—about 200°C .—but is not quite pure, being usually mixed with Chlorine. This is, however, the best way to prepare the gas, and, if collected over water (Fig. 15), most of the Chlorine dissolves. If the solid left at the end of the experiment is mixed with water, the Potassium

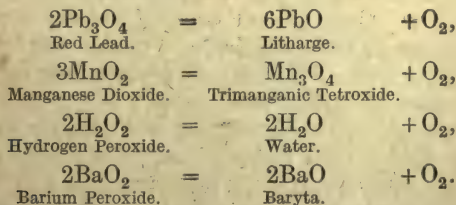
Chloride dissolves, and the residue is found to consist of Manganese Dioxide ; it can be filtered from the solution of Potassic Chloride, dried and weighed, and, if a weighed quantity has been taken at the beginning of the experiment, exactly the same quantity is found to be present at the end.

It appears, then, as if it had taken no part in the reaction itself, but by its mere presence had accelerated the velocity of decomposition. Substances which behave in this manner are by no means uncommon ; for example, Ferric Oxide, Copper Oxide or Nickel Oxide, might have been used instead of Manganese Dioxide in the above experiment,—and to them the name of *Catalytic Agent* or *Catalyst* has been given, while the process is called *Catalysis*.

It is probable that in many of the cases of Catalysis the Catalyst undergoes change during the progress of the reaction, but is reproduced unchanged at the end of the reaction. The action of a Catalyst has been compared by Ostwald with the action of oil on a machine, or a whip on a sluggish horse ; he also maintains that the reaction must be in progress before the Catalyst can act, but this is not quite in accordance with all the facts.

A *Catalyst*, then, may be defined as a substance which can start or accelerate the velocity of a chemical reaction.

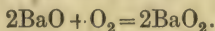
(3) Oxygen is always evolved when the class of compounds known as Peroxides is heated ; amongst these are Red Lead, Manganese Dioxide (at 400° C.), Hydrogen Peroxide and Barium Peroxide. The reactions which occur are indicated by the following equations :



The last mentioned process is the one used in the commercial preparation of Oxygen by Brin's process (1881).

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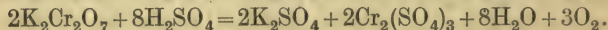
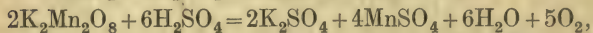
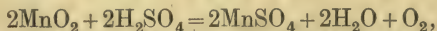
When Barium Dioxide is heated to a temperature of about 800°C ., it yields up half of its Oxygen forming the Monoxide, as in the above equation, while the Monoxide, if kept at a temperature of 500°C . and brought into contact with air or Oxygen, absorbs the Oxygen forming the Dioxide, thus :



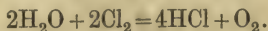
These reactions formed the basis of the process, but in actual practice it was found difficult to regulate the temperature with sufficient accuracy for economical production ; this difficulty was overcome when it was discovered that by keeping the temperature constant at 700°C . and changing the pressure, the Monoxide absorbed Oxygen under a pressure of two atmospheres, while the Dioxide evolved the Oxygen when the pressure was reduced to $\frac{1}{20}$ atmosphere.

This process is now rapidly becoming obsolete, most of the Oxygen made industrially being obtained from liquid air.

(4) Another method for preparing Oxygen is by the action of warm strong Sulphuric acid on Peroxides, Permanganates or Bichromates, thus :



(5) It may be obtained from water, by passing a mixture of Steam and Chlorine gas through a porcelain tube containing broken fragments of porcelain, heated to redness in a furnace,



The Properties of Oxygen. Oxygen is a colourless, odourless gas, slightly heavier than air ; it dissolves sparingly in cold water—100 c.c. of water dissolves 5 c.c. of the gas at 0°C . and 760 mm.—and it is upon this dissolved Oxygen that fishes depend for their breathing. It is, of course, essential for the respiration of all animals, and is administered in cases of prostration or suffocation, when, owing to the weak action of the lungs, the blood is not sufficiently aerated. Pure Oxygen,

if breathed for some time, raises the body temperature very considerably, and eventually causes death. It is absorbed by the metals Silver, Gold and Platinum, at high temperatures, but is evolved again as the metal cools.

It can be liquefied, forming a bluish coloured liquid at a temperature of -119°C . under a pressure of 50 atmospheres. The liquid is strongly magnetic, and in some ways is not so active as gaseous Oxygen, as it has no action on Phosphorus, Potassium or Sodium.

Gaseous Oxygen is chemically very active, most elements unite directly with it, especially if hot, forming their Oxides; Sulphur, Phosphorus, Iron, Magnesium and Sodium burn brilliantly in an atmosphere of Oxygen, but the presence of a small quantity of water vapour is a necessity for their combustion to take place.



FIG. 14.—Water vapour as a catalytic agent.

This may be shewn by taking a tube shaped as in the diagram (Fig. 14), placing a small piece of Phosphorus at *A*, some Phosphorus Pentoxide powder at *B*, filling the tube with pure Oxygen, and sealing it up at *C*. If this tube is left for a few days, the Phosphorus Pentoxide abstracts all the moisture from the Oxygen, and then the Phosphorus may be strongly heated and distilled from one part of the tube to another without catching fire.

Water then acts as a catalytic agent in many combustions. The combustion of Iron in Oxygen may be well shewn by holding a strip of steel watch spring in front of an Oxy-Coal-gas blow pipe; as soon as the combustion commences, the supply of coal gas is shut off and the metal continues to burn in the jet of Oxygen with remarkable brilliance. The black Oxide of Iron left is called the magnetic Oxide Fe_3O_4 .

OXIDES.

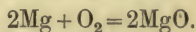
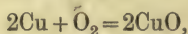
The compounds formed by the union of Oxygen with other elements are called Oxides; they vary considerably in their properties, and are usually divided into four classes: (1) Acidic Oxides; (2) Basic Oxides; (3) Peroxides; (4) Neutral Oxides.

Acidic Oxides. These are nearly all Oxides of non-metals, though a few of the higher Oxides of the metals belong to this class. Examples are: Sulphur Dioxide SO_2 , Sulphur Trioxide SO_3 , Nitrogen Pentoxide N_2O_5 , Phosphorus Pentoxide P_2O_5 , and Silica SiO_2 among the non-metallic oxides; and Chromium Trioxide CrO_3 and Manganese Heptoxide Mn_2O_7 among the Oxides of metals. Many of them, but by no means all, can be prepared by heating the element in Oxygen.

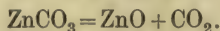
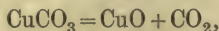
Most of them dissolve in water; the solutions thus formed turn blue litmus red, evolve Carbon Dioxide when placed upon Sodium Carbonate Na_2CO_3 , and many of them evolve Hydrogen gas when treated with powdered Magnesium.

Basic Oxides. These are *all* oxides of metals, and may be prepared in various ways:

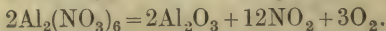
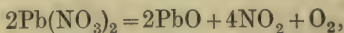
- (1) By heating the metal in air or in Oxygen.



- (2) By heating the Carbonate of the metal; Carbon Dioxide gas is evolved and the basic Oxide left.

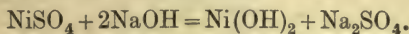


- (3) By heating the Nitrate of the metal; Nitrogen Peroxide gas and Oxygen are evolved and the basic Oxide left.



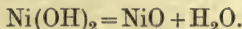
- (4) By heating the Hydroxide of the metal; this compound is

usually precipitated when a solution of Caustic Soda is added to a soluble salt of the metal, thus :



↓

Heat merely drives off the water, leaving the basic Oxide :



Only a few basic Oxides—those of Potassium, Sodium and Calcium being amongst the number—are soluble in water; such solutions turn red litmus blue, and they evolve no gases either with Sodium Carbonate or Magnesium powder.

When excess of a basic Oxide, which is insoluble in water, is boiled with a dilute acid for some time, part of the Oxide is dissolved; the liquid loses its acid properties and will no longer turn blue litmus red; a Salt is formed, and the acid is said to be neutralized.

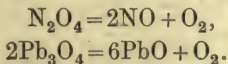
Peroxides. These are usually Oxides of metals containing a greater percentage of Oxygen than their basic Oxides.

Examples.

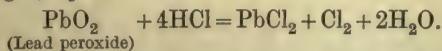
PEROXIDES.	CORRESPONDING BASIC OXIDES.
Barium Dioxide, - BaO_2 .	Baryta, - - BaO .
Red Lead, - - Pb_3O_4 .	Litharge, - - PbO .
Sodium Peroxide, - Na_2O_2 .	Sodium Oxide, - Na_2O .
Manganese Dioxide, MnO_2 .	Manganous Oxide, MnO .

One or two Peroxides are oxides of non-metals, such as Chlorine and Nitrogen Peroxides, ClO_2 and N_2O_4 .

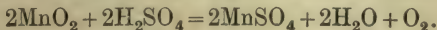
All Peroxides give off Oxygen when heated, leaving an Oxide containing a smaller percentage of Oxygen, thus :



When warmed with strong Hydrochloric acid, they yield Chlorine gas, *e.g.* :



When heated with strong Sulphuric acid Oxygen is evolved.



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Neutral Oxides. A few oxides are known, mostly non-metallic, which do not give the reactions of either Acidic, Basic or Peroxides; they are usually called Neutral Oxides. Examples of this class are Carbon monoxide CO , Nitric Oxide NO and Water H_2O .

Instances are known of Oxides which apparently belong to two classes; thus Lead Peroxide PbO_2 has all the reactions of the Peroxides, and, in addition, with Hydrochloric acid under certain conditions yields a salt, Lead Tetrachloride PbCl_4 , and must therefore be considered a basic Oxide. For this class of Oxides the name "Amphoteric" has been suggested.

PROBLEMS.

2. What weight of Trimanganic Tetroxide is left behind when 3 grams of Manganese Dioxide are heated to bright redness?
3. Determine the volume of Oxygen given off when 5 grams of Potassium Chlorate are heated; the gas is collected at 12°C . and 772 mm.
4. 2.5 grams of Lead Nitrate are strongly heated; what weight of Lead Oxide remains?

PRACTICAL EXERCISES.

To find the percentage of Oxygen in Potassic Chlorate. Weigh a clean dry test tube made of hard glass; weigh into it about one gram of powdered Potassic Chlorate. Heat the tube and its contents till all effervescence ceases and the mass again becomes solid, being careful to heat that part of the solid which usually resolidifies some little distance up the tube. When cool, weigh again, and the loss in weight gives the Oxygen in the weight of Potassic Chlorate originally taken, whence the percentage can be calculated.

A good result should be about 39 per cent.

To find the Weight of a Litre of Oxygen Gas at the Temperature and Pressure of the Laboratory. Take a hard glass test tube, and fit a cork and delivery tube, as in the diagram. Crush some Potassium Chlorate in a mortar, and put it into the bottom of the tube, and above it place a small wad of asbestos wool. Weigh the tube and contents without the cork. Attach a

rubber tube *B* to the end of the delivery tube, and insert it through a bee-hive shelf into a graduated gas jar, as in the diagram (Fig. 15). Now heat the Chlorate, so as to drive off Oxygen. Do this cautiously, so as not to fill the cylinder entirely. When it is nearly full stop the action, and cool the cylinder *A* by pouring water over it. When cold, slip out the tube *B*, put a plate over the mouth of the cylinder, and transfer it to a deep vessel of water to adjust the level inside and out. Read the volume of the gas. Remove the cork from the test

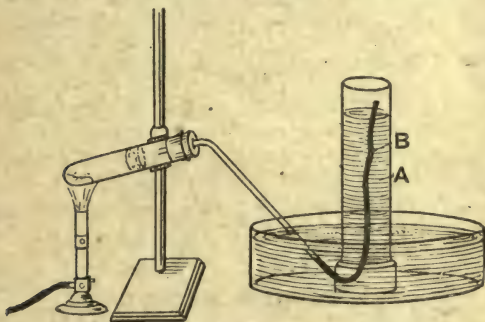


FIG. 15.—To find the weight of 1 litre of Oxygen.

tube, and when cold weigh the tube and contents again. The loss of weight represents the weight of the Oxygen collected, and from this is found the weight of 1000 c.c.

N.B.—You have collected in the cylinder a small quantity of air as well as Oxygen. This air was contained in the tubes before the heat was applied. But these tubes are now full of Oxygen, so that the error is the difference between the weights of air and Oxygen which the tubes would contain. This is small enough to be neglected.

A good result would be near 1.44 grams.

To ascertain whether a given Oxide is Acidic, Basic or a Peroxide.

Test (1). If possible, dissolve some of the Oxide in water and test the solution with litmus paper. If it turns blue litmus red, the Oxide is Acidic ; if red, blue, the Oxide is Basic.

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Test (2). Heat a little of the Oxide in a small test tube and test for Oxygen by means of a glowing splinter. If Oxygen is evolved, it is a Peroxide, unless it is red in colour and deposits Mercury globules on the cool sides of the tube, when it is Mercuric Oxide, which is Basic.

Test (3). Take about one inch depth of *dilute* Nitric acid in a test tube and keep adding the Oxide, little by little, till no more dissolves, even on boiling. Test the liquid with blue litmus paper, and if it is no longer reddened, the Oxide is Basic.

Test (4). Warm a little of the Oxide with strong Hydrochloric acid ; if Chlorine gas is evolved, which may be recognized by its smell and bleaching action on litmus paper, the Oxide is a Peroxide.

CHAPTER IV.

ACIDS, BASES AND SALTS.

THE difference in the properties of the classes of substances called Acids and Alkalies was recognized in the earliest times.

Robert Boyle (1680) gave as the characteristic properties of Acids: (1) a sour taste, (2) great solvent power, (3) change blue vegetable dyes (*e.g.* litmus) red, (4) lose these properties when combined with Alkalies.

Alkalies, he said, (1) possessed soapy properties, (2) dissolved oils and Sulphur, (3) restored the colours of vegetable dyes changed by Acids, (4) lost these properties when combined with Acids.

It is thus seen that the properties of Acids and Alkalies are opposed to one another, for, when mixed, they lose their characteristic properties, forming neutral substances to which the name of Salts was given owing to common salt being an important member of the class.

Later, a class of earthy bodies was discovered which acted towards Acids like Alkalies, though they did not dissolve in water and had no effect on vegetable dyes. The name Base was employed by Rouelle (1744) to include these earthy bodies, the Alkalies and metallic calces, all of which react with Acids to form Salts.

Acids. It has already been seen that Acidic Oxides dissolve in water, forming Acid solutions. Lavoisier (1777), realizing this, concluded that Oxygen is an element common to all Acids, and that its presence constitutes or produces their

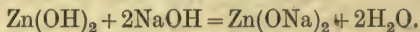
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Acidity. Hence he gave to Oxygen its name, which means Acid-producer.

That this was a misnomer was soon made plain, for Oxides were known (such as Lime) whose solutions in water did not possess Acid properties, in fact, were Alkaline in their effects; also Berthollet (1787) shewed that Prussic acid (HCN) contained no Oxygen, a similar proof with regard to Hydrochloric and Hydriodic acids being established a little later by Sir Humphrey Davy.

A loose definition of an Acid may be arrived at by saying that they usually have a sour taste, are corrosive, redden blue litmus and contain Hydrogen, part or the whole of which can be replaced by a metal when the Acid is acted upon by "dilute" Alkalies.

Now strong solutions of an Alkali like Caustic Soda will act upon solutions containing Aluminium or Zinc Hydrates, and cause the Hydrogen in them to be replaced by Sodium, thus:



But these Zinc and Aluminium Hydrates are far from being recognized as Acids, hence the inclusion of the word "dilute" in the above definition. Again, a solution of ordinary Alum is sour, fairly corrosive, and reddens blue litmus, but it has no replaceable Hydrogen, and so cannot be called an Acid.

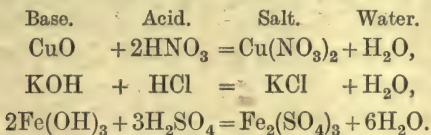
Basicity of Acids. The number of replaceable Hydrogen atoms in a molecule of an Acid is termed its Basicity. Acids, then, may be mono-, di-, tri-, or tetrabasic according as they contain one, two, three or four atoms of Hydrogen in their molecule which are replaceable by a metal. Hydrochloric acid HCl and Nitric acid HNO_3 are naturally monobasic, as their molecules contain but one Hydrogen atom each. Acetic acid $\text{C}_2\text{H}_4\text{O}_2$ is also monobasic, as only one of its four Hydrogen atoms is replaceable by a metal.

Sulphuric acid H_2SO_4 and Oxalic acid $\text{C}_2\text{H}_2\text{O}_4$ can replace both their Hydrogen atoms, and so are dibasic, as also is Tartaric acid $\text{C}_4\text{H}_6\text{O}_6$, which can only replace two of its six Hydrogen atoms.

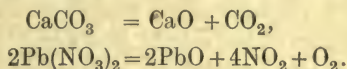
Bases. Bases are always Oxides or Hydroxides of metals.

When soluble in water they have a bitter taste, turn red litmus blue and are called Alkalies. Whether soluble in water or not, they react with Acids to form neutral bodies—Salts—and water *only*.

This last is their most important property, and a few examples in the way of chemical equations are appended :



The term Base was originally applied to these metallic Oxides because they were the foundation, as it were, of a salt, being the portion of it left behind, in many cases, when the salt was strongly heated, *e.g.* :



Salts. When all, or part, of the Hydrogen in an Acid is replaced by a metal, a Salt is produced.

Salts are usually divided into three classes : Normal salts, Acid salts and Basic salts.

In *Normal* salts the whole of the available Hydrogen atoms are replaced by a metal, *e.g.* Potassium Sulphate K_2SO_4 and Sodium Oxalate $(\text{COONa})_2$.

In *Acid* salts part only of the Hydrogen in the acids is replaced by a metal, and the salt still contains replaceable Hydrogen, *e.g.* Potassium Hydrogen Sulphate KHSO_4 and Sodium Hydrogen Phosphate Na_2HPO_4 .

The term Acid Salts, as usually applied, is, in a way, misleading, for many of them do not possess the recognized property of Acids by reddening blue litmus, though most of them do. Sodium Hydrogen Phosphate Na_2HPO_4 , for instance, is practically neutral, whilst Sodium Hydrogen Carbonate NaHCO_3 is alkaline in its effects.

Sometimes the term Hydrogen Salts is applied to them, or the prefix bi- or di- is added to the name of the salt, *e.g.* NaHSO_4

is called Sodium Acid Sulphate, Sodium Hydrogen Sulphate or Sodium Bisulphate.

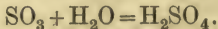
Basic Salts are normal salts chemically combined with Bases; they are not of very common occurrence. Examples are Basic Copper Carbonate $\text{CuO} \cdot \text{CuCO}_3$, Basic Bismuth Chloride $\text{BiCl}_3 \cdot \text{Bi}_2\text{O}_3$, $[\text{BiOCl}]$, often called Bismuth Oxychloride, and Basic Lead Acetate $\text{PbO} \cdot \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

It must not be understood that Normal Salts are always neutral bodies with regard to their action with litmus; this is far from being the case. Sodium Carbonate Na_2CO_3 and Sodium Borate $\text{Na}_2\text{B}_4\text{O}_7$, for instance, are alkaline, whilst Copper Sulphate CuSO_4 and Aluminium Chloride AlCl_3 are acid in this respect.

This is due to the fact that the union of a "strong" acid (p. 171) with a "weak" base will often produce a salt which reddens blue litmus, whilst the union of a "weak" acid and "strong" base has the opposite effect.

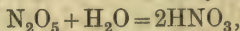
The Preparation of Acids. Practically all Acids can be obtained by dissolving the Acidic Oxides contained in them in water. These Oxides are, for this reason, often called the Anhydrides of their respective Acids.

For example, Sulphur Trioxide dissolves in water, forming Sulphuric acid.



SO_3 is called Sulphuric Anhydride.

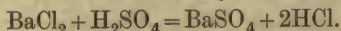
Again, Nitrogen Pentoxide in water yields Nitric acid.



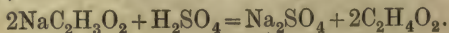
hence N_2O_5 is called Nitric Anhydride.

This method is, of course, not applicable to Hydracids, the term usually applied to Acids like Hydrochloric HCl , Hydrocyanic HCN and Hydrosulphuric H_2S , which contain no Oxygen; these, and many other Acids, may be driven from their salts by a less volatile acid.

For example, Sulphuric acid will, on heating, cause Hydrochloric acid to be driven out of any Chloride such as Barium Chloride.



Similarly, Sodium Acetate and Sulphuric acid yield Acetic acid.

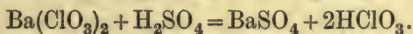


Acids prepared in this manner are usually condensed from a state of vapour by cooling.

It is sometimes thought that this action represents the turning out, from a salt, of a weak acid by a strong one, but, according to the modern accepted definition of strong and weak acids, this is not the case, for Hydrochloric acid is considered to be a stronger acid than Sulphuric acid.

It is merely that, at the temperature of the reaction, the acid driven off is more volatile than the other acid present, which remains behind in the salt.

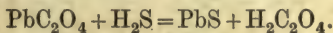
Many acids, such as Chloric HClO_3 , Hydriodic HI , etc., are decomposed by strong Sulphuric acid, but they may be prepared, when their Barium salt is soluble in water, by adding enough dilute Sulphuric acid to exactly precipitate all the Barium present as insoluble Barium Sulphate, thus :



↓

When the Barium salt is insoluble in water, the corresponding Lead salt is used ; this, even if insoluble in water, may be suspended in that liquid, and then, when Sulphuretted Hydrogen gas is bubbled through the liquid, insoluble Lead Sulphide separates out as a black precipitate and the acid is left in solution.

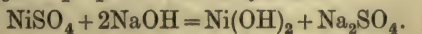
Thus, to prepare Oxalic acid, Sulphuretted Hydrogen is bubbled through Lead Oxalate suspended in water.



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The Preparation of Bases. Bases are Oxides or Hydroxides of metals.

The preparation of Basic oxides has already been given. Hydroxides of all the commoner metals, except Sodium, Potassium, Calcium, Strontium and Barium, are precipitated when a solution of Caustic Soda (or Potash) is added to a solution of any of their soluble salts. When filtered and washed, these precipitated Hydroxides form Bases very readily soluble in Acids ; *e.g.* to prepare Nickel Hydroxide :—



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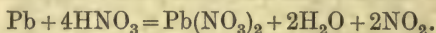
The Preparation of Salts. Normal salts are prepared in several ways.

(1) *By the direct action of the Acid upon the metal.* This has only a limited application, as comparatively few Acids are capable of dissolving metals. In practice, the metal is added to the dilute Acid, till no further evolution of gas occurs, even on warming; the solution is poured off from the excess of metal, which must be present, is concentrated by evaporation and, when possible, the salt is crystallized out.

For example, to prepare Zinc Sulphate from Zinc and dilute Sulphuric acid,

$$\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2.$$

And Lead Nitrate from Lead and dilute Nitric acid,

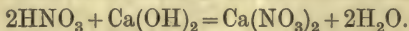


(2) *By the action of Alkalies, i.e. Soluble Bases, on Acids.* This method, also, has only a limited application, as so few of the Bases are soluble in water. The solutions of Acid and Alkali are mixed, till the resulting liquid has a neutral effect upon litmus paper; it is then evaporated and the salt crystallized out, if possible.

Examples. Potassium Sulphate from Caustic Potash and dilute Sulphuric acid.

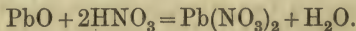


Calcium Nitrate from Nitric acid and Lime water.

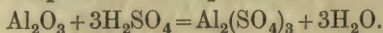


(3) *By the solution of Basic oxides in Acids.* This method admits of almost universal application, and is the one generally adopted. The Basic Oxide is added to the warmed dilute acid till no more will dissolve, the excess of Oxide is then filtered away and the salt obtained from the filtrate as before.

Examples. Lead Nitrate from Nitric acid and Litharge.



Aluminium Sulphate from Sulphuric acid and Alumina.

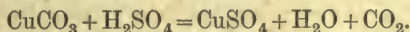


(4) *By the solution of the Carbonates of metals in Acids.* This method is often valuable, as the Carbonates are, in some

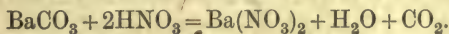
cases, more readily soluble in the Acids than the Basic Oxides. The method of procedure is exactly as in (3), Carbon Dioxide gas being evolved during the operation.

N.B.—Only Carbonates which are insoluble in water must be used.

Examples. Copper Sulphate from Copper Carbonate and Sulphuric acid.

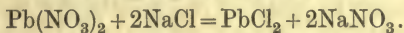


Barium Nitrate from Barium Carbonate and Nitric acid.



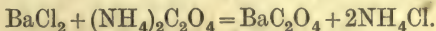
(5) *By precipitation.* This method can only be employed when the required salt is insoluble in water or whatever solvent is present. The salt is separated out by Double Decomposition—the name given to the interchange of the Acid radicles of two metallic salts when their solutions are mixed—filtered, washed and dried.

Examples. Lead Chloride from Lead Nitrate and Common Salt.



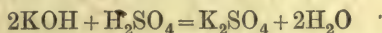
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Barium Oxalate from Barium Chloride and Ammonium Oxalate.

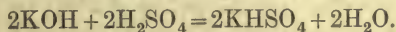


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The Preparation of Hydrogen Salts. The reaction indicated by the equation



shows the preparation of Normal Potassium Sulphate. That for the preparation of the Hydrogen salt is given by

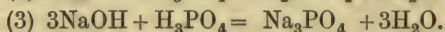
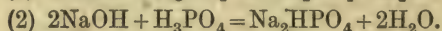
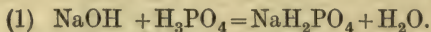


From this it is clear that the Hydrogen salt of a dibasic acid can be prepared by adding to the same quantity of Base double the quantity of Acid necessary for the Normal salt. This method is applicable only when the Normal salt is neutral to litmus, and, of course, does not apply in the case of the Carbonates and Bicarbonates of Sodium and Potassium, which are both Alkaline.

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The case of the Hydrogen salts of the tribasic Orthophosphoric acid H_3PO_4 is interesting.

Their preparation from Base and Acid is shewn in the equations :



Of these three Phosphates, the di-Sodium mono-Hydrogen Phosphate Na_2HPO_4 (ordinary Sodium Phosphate of the chemist) is practically neutral to litmus, NaH_2PO_4 being Acidic and Na_3PO_4 being Alkaline in their reactions.

To prepare Na_2HPO_4 , then, it is necessary simply to neutralize the Caustic Soda solution with dilute Phosphoric acid in the ordinary way, noting the amounts of each solution necessary for neutralization, and crystallize the resulting liquid. For NaH_2PO_4 the same quantity of Caustic Soda is taken and double the quantity of Phosphoric acid, whilst for Na_3PO_4 the same quantity of Phosphoric acid solution is taken and $1\frac{1}{2}$ times that of the Caustic Soda solution used in the first case.

PROBLEMS.

5. What weight of Copper Sulphate crystals ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) can be theoretically obtained by dissolving 5 grams of Copper Carbonate in dilute Sulphuric acid ?

6. Excess of Barium Chloride solution is added to 50 grams of a 5 per cent. solution of Sulphuric acid ; what weight of Barium Sulphate is thrown down ?

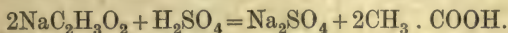
7. Dilute Nitric acid is added to 40 grams of a 10 per cent. solution of Caustic Potash till the liquid reddens blue litmus ; the liquid is then evaporated to dryness ; what weight of Saltpetre is left ?

PRACTICAL EXERCISES.

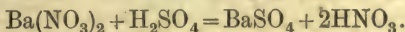
To prepare Acids from Salts which contain them.

(1) *Acetic acid from Sodium Acetate.* Take 10 grams of Sodium Acetate in a retort, cover with strong Sulphuric acid, and distil over about 5 c.c. of liquid into a small flask cooled

by water. This liquid is Acetic acid. Test it for Sulphuric acid, which may be an impurity, by adding Barium Chloride solution, which should produce no precipitate if it is pure.

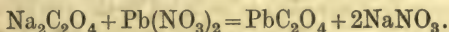


(2) *Nitric acid from Barium Nitrate.* Add dilute Sulphuric acid gradually to a solution of Barium Nitrate, till, after allowing the precipitate to settle, further addition of the acid produces no turbidity. Filter away from the precipitated Barium Sulphate and the filtrate is dilute Nitric acid.



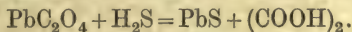
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(3) *Oxalic acid from Sodium Oxalate.* Dissolve the Sodium Oxalate in water and add excess of Lead Nitrate solution. This produces a white precipitate of Lead Oxalate.



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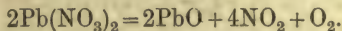
Filter the liquid, make a hole in the bottom of the filter paper with a glass rod and wash the Lead Oxalate through into a boiling tube. Pass Sulphuretted Hydrogen through the turbid liquid in the boiling tube for 5 minutes. Filter from the precipitated Lead Sulphide, and the filtrate, if concentrated by boiling, should deposit crystals of Oxalic acid.



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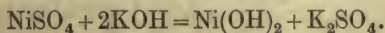
To prepare Bases from Salts which contain them.

(1) *Lead Oxide from Lead Nitrate.* Crush the Lead Nitrate in a mortar, and place a few grams of it in a porcelain crucible. Heat strongly, with the lid on, and Litharge will be left in the crucible.



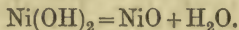
N.B.—Test the escaping gases for Oxygen.

(2) *Nickel Oxide from Nickel Sulphate.* Dissolve the Nickel Sulphate in water, precipitate Nickel Hydrate from the solution by adding Caustic Potash.



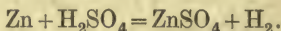
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Filter, wash the precipitate on the filter paper and dry on a cone over a sand bath. When dry, remove the precipitate from the filter paper to a porcelain crucible and heat; Nickel Oxide is left.

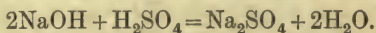


The Preparation of Salts.

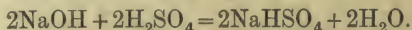
(1) *Zinc Sulphate from Zinc and Sulphuric acid.* Take 50 c.c. of dilute Sulphuric acid in a beaker, and add about 20 grams of granulated Zinc. When action has ceased, filter from the excess of Zinc into a porcelain dish, evaporate half the liquid away and allow to crystallize.



(2) *Sodium Sulphate from Caustic Soda and Sulphuric acid.* Take dilute solutions of Caustic Soda and Sulphuric acid in two beakers. Place about 20 c.c. of the Acid in a porcelain dish and add the Alkali carefully, testing, from time to time, by taking out a drop on the end of a glass rod and placing it upon litmus paper. When the liquid has no effect either on blue or on red litmus paper, concentrate to about one-third of the original amount, and allow to crystallize. These crystals are those of the Normal Sodium Sulphate.

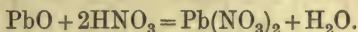


(3) *Sodium Hydrogen Sulphate from Caustic Soda and Sulphuric acid.* Use the same solutions as in the last experiment. Place about 25 c.c. of the Caustic Soda solution in a porcelain dish, and put the Sulphuric acid in a burette. Add the Acid gradually till the liquid in the dish is neutral, testing as before. Note how much Acid has been added, and add exactly the same quantity in excess. Concentrate to one-third of the original amount and allow to crystallize. The crystals are those of Sodium Hydrogen Sulphate.

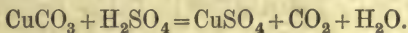


(4) *Lead Nitrate from Litharge and Nitric acid.* Take about 30 c.c. of dilute Nitric acid in a beaker, warm gently, and add Litharge till no more is dissolved. Filter from the excess of

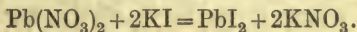
Litharge, concentrate if necessary and allow to cool. The crystals are Lead Nitrate.



(5) *Copper Sulphate from Copper Carbonate and dilute Sulphuric acid.* Proceed exactly as in No. 4, putting dilute Sulphuric acid in the beaker and adding Copper Carbonate.



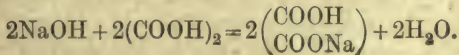
(6) *Lead Iodide from Lead Nitrate and Potassium Iodide.* Mix dilute solutions of Lead Nitrate and Potassium Iodide together in a beaker; a yellow precipitate of Lead Iodide is formed. Boil till the precipitate is all dissolved, adding more water if necessary, and allow to cool. Crystals of Lead Iodide separate out, and may be purified by washing with *cold* water.



↓

To determine the Basicity of Oxalic acid. Take 25 c.c. of a solution of Caustic Soda in a porcelain dish and add Oxalic acid solution from a burette till the liquid is neutral to phenolphthalein. Concentrate the solution to obtain crystals.

Repeat the experiment with the same amount of Caustic Soda solution, but adding exactly twice as much Oxalic acid as before. Crystallize the resulting liquid, and compare the two sets of crystals obtained under the microscope. They will be found to be different in shape, shewing that two different salts have been obtained and that Oxalic acid is dibasic.



CHAPTER V.

ALKALIMETRY AND ACIDIMETRY.

THE neutralization of "strong" (see p. 171) Acids by "strong" Alkalies forming Salts, which are neutral to Litmus, is made the basis of very important processes for estimating the strength of solutions of Acids and Alkalies.

This is most valuable, because the accurate weighing of pure Acids and Alkalies, such as Hydrochloric, Sulphuric and Nitric acids or Caustic Soda and Potash, is very difficult—the first mentioned since it is a gas, and the others because they readily absorb water during weighing, and are therefore never quite pure.

Richter (1790-1800) shewed that the weights of various Acids, which neutralize a fixed weight of one of the Bases, are the same for certain fixed weights of all the Bases. This he called the Law of Proportionality.

It is perhaps best illustrated by the following table :

Acids.		Bases.	
HCl,	36.5.	NaOH,	40.
H ₂ SO ₄ ,	49.	KOH,	56.
HNO ₃ ,	63.	Ca(OH) ₂ ,	37.

The numbers opposite the various Acids and Alkalies represent the fixed proportions in which they will neutralize one another; *e.g.* 40 grams of Caustic Soda will neutralize 36.5 grams of Hydrochloric acid or 49 grams of Sulphuric acid or 63 grams of Nitric acid, and similarly any of the Acids or Alkalies may be taken. These numbers are called the *Equivalent Weights* of the Acids or Alkalies.

These Equivalent Weights, it must be noted, contain one gram of Hydrogen in the Acids, and the Equivalent Weight of the metals contained in the Alkalies. It follows from this that, if a solution of any Acid (or Alkali), whose strength is known, is obtained, the strength of another solution of Alkali (or Acid) can be ascertained, by a determination of the proportions, by volume, in which these solutions neutralize one another.

In performing Neutralization experiments—they are called *Titrations*—the Acid solution is added from a burette to a known volume (say 25 c.c.) of the Alkaline solution contained in a beaker; to the latter a few drops of Litmus are added to indicate the point of neutralization, and one drop of Acid added from the burette should change the colour of the Litmus from blue to red when neutralization is complete.

N.B.—It will be noticed that a slight error is introduced here, as a small excess, limited to one drop in an accurate experiment, of Acid has been added to turn the Litmus; but, as a rule, the solutions used are so dilute that this error may be neglected.

Other indicators, *e.g.* Methyl orange, may be used instead of Litmus; it possesses the advantage of not changing its colour when Carbonic acid is present, but it is not so reliable, or so sensitive, as Litmus.

Example of a Titration. 25 c.c. of a solution of Caustic Soda, containing 20 grams of Caustic Soda per litre, were found to require 22·5 c.c. of a solution of Sulphuric acid for exact neutralization; required, the strength of the latter in grams per litre.

Every c.c. of the Caustic Soda solution contains ·02 gram of Caustic Soda, so 25 c.c. will contain $25 \times \cdot 02 = \cdot 5$ gram of Caustic Soda.

From the Equivalent Weights, 40 grams of Caustic Soda neutralize 49 grams of Sulphuric acid; therefore ·5 gram of NaOH require $\cdot 5 \times \frac{49}{40} = \cdot 6125$ gram of H_2SO_4 for neutralization.

This weight of Sulphuric acid must, therefore, be contained in the 22·5 c.c. of the solution added from the burette.

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If 22.5 c.c. of this solution contain .6125 gram of H_2SO_4 , 1 litre must contain $.6125 \times \frac{1000}{22.5} = 27.2$ grams of H_2SO_4 .

Of course, since the colour of the Indicator is changed, a small quantity of Acid must have been added in excess of the exact quantity required for neutralization. This is unavoidable, but, if the solutions are made sufficiently dilute, the error will not exceed 1 part in 1000.

For convenience in simplifying the calculations, solutions are made up in Normal strengths; such solutions contain the equivalent weight of the Acid or Alkali in grams dissolved in 1 litre of the solution, and are denoted by the prefix N, *e.g.* N. H_2SO_4 solution contains 49 grams of Sulphuric acid per litre of solution, and N. KOH solution contains 56 grams of Caustic Potash per litre.

When greater accuracy is required, solutions may be made up in deci-normal $\left(\frac{N}{10}\right)$ or even in centi-normal $\left(\frac{N}{100}\right)$ strengths; centi-normal Caustic Soda, for example, would contain .4 gram of Caustic Soda per litre. Normal solutions of Acids and Alkalies will, clearly, neutralize one another in equal volumes, as will $\frac{N}{10}$ or $\frac{N}{100}$ solutions. 1 c.c. of any Normal solution of an Acid will neutralize 1 c.c. of any Normal solution of an Alkali, and will be equivalent in neutralizing power to 1 c.c. of a Normal solution of any other Acid.

Example. 25 c.c. of a Caustic Potash solution required 15 c.c. of a Normal Sulphuric acid solution for neutralization; in another titration the same quantity of the same Alkaline solution required 17.5 c.c. of a Hydrochloric acid solution of unknown strength; find the strength of the latter solution. Of the two Acid solutions it is clear that the Hydrochloric acid is the weaker, being $\frac{15}{17.5}$ of the strength of the Sulphuric acid solution.

But the Sulphuric acid solution is of Normal strength. Therefore the Hydrochloric acid solution is $\frac{15}{17.5}$ Normal

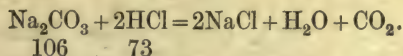
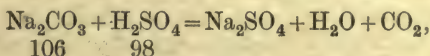
strength. Now N. HCl contains 36.5 grams per litre, hence the above solution must contain $\frac{15}{17.5} \times 36.5 = 31.28$ grams of Hydrochloric acid per litre.

It will be seen from the above that, once an accurately made solution of Acid or Alkali has been established, the strengths of any other Alkalies or Acids can be ascertained by using it.

The preparation of an accurate solution of the ordinary Acids or Alkalies is, for reasons mentioned before, a matter of extreme difficulty; this may be surmounted by using Sodium Carbonate (Na_2CO_3) as the basis of the experiments. This substance neutralizes Acids in a similar manner to Caustic Alkalies, with the exception that Carbonic acid gas is formed in the operation and part of it remains in the solution, changing the colour of the Indicator if Litmus is used.

Consequently, either the liquid must be boiled, when the Carbonic acid gas is expelled and the Litmus resumes its original colour, or another Indicator, such as Methyl orange, must be used.

The reactions of Sodium Carbonate with Sulphuric and Hydrochloric acids are shewn by the equations:



Since the equivalent weights of Sulphuric and Hydrochloric acids are 49 and 36.5 respectively, and these quantities of the Acids each neutralize 53 grams of Sodium Carbonate, it follows that the equivalent weight of Sodium Carbonate is 53, and Normal Sodium Carbonate solution contains 53 grams of Sodium Carbonate per litre.

As Sodium Carbonate can be obtained in a high state of purity, the making of such a solution presents no difficulty, and, by using it, other Acid and Alkaline solutions can be standardized.

PROBLEMS.

8. 25 c.c. of a Caustic Soda solution required 18.5 c.c. of N. HCl for exact neutralization. The same quantity of the Alkali required 20 c.c. of a solution of Sulphuric acid to neutralize it. Find the strength of the Sulphuric acid solution in grams per litre.

9. 10 c.c. of a solution of Caustic Potash required (a) 14.3 c.c. of $\frac{N}{10}$ H_2SO_4 , (b) 12.7 c.c. of an Oxalic acid solution for complete neutralization. Find the strength of the Oxalic acid solution.

10. How many c.c. of N. H_2SO_4 must be added to 50 c.c. of a Caustic Soda solution containing 60 grams per litre, in order to obtain a pure specimen of Sodium Hydrogen Sulphate?

PRACTICAL EXERCISES.

To prepare a Normal Solution of Sodium Carbonate. The equivalent weight of Sodium Carbonate is 53 grams. To make up 250 c.c. of N. Na_2CO_3 , take about 20 grams of Anhydrous Sodium Carbonate in a porcelain dish, and heat strongly over a bunsen burner till it is quite dry, and allow to cool in a desiccator. While it is cooling weigh a beaker accurately, and then weigh into it exactly 13.25 grams of the dry Sodium Carbonate. Dissolve this solid in about 100 c.c. of distilled water and, when all is dissolved, pour the contents of the beaker into a clean measuring flask which holds 250 c.c.; wash the beaker at least twice with distilled water, pouring the washings carefully into the flask. Then fill the flask exactly up to the mark, *shake the contents well*, and the result is N. Na_2CO_3 solution.

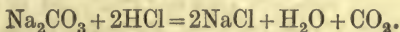
To find the Strength of a Solution of Hydrochloric Acid and to prepare from it N. HCl. To do this it is necessary to take the given solution of Hydrochloric acid, and neutralize it with the N. Na_2CO_3 solution prepared in the last experiment, ascertaining exactly the number of c.c. of Acid solution required.

In these Acid and Alkaline titrations the most accurate results are obtained by placing the Acid solution in a burette and adding it to a known quantity of the Alkaline solution contained in a beaker.

N.B.—Burettes and pipettes used in Volumetric Analysis must always be rinsed out, before filling, with a few c.c. of the solution to be placed in them: this is because, when put away, they always have a little water adhering to the sides, and this would make weaker any solution which was placed in them. A burette or pipette thus rinsed out is said to be “clean” for that particular solution.

To perform the titration, “clean” a burette with the Hydrochloric acid solution, and fill it up to the zero mark with the same, being especially careful to get rid of all air bubbles at or near the top of the burette; next, “clean” a 10 c.c. pipette, and fill it with the $N. Na_2CO_3$ solution, and let the contents run out into a beaker, which has previously been rinsed out with distilled water. Then add to the liquid in the beaker one or two drops of strong litmus solution—enough to enable you to see the blue colour—to act as an “indicator” of the point when neutralization is complete.

Now add gradually, a few drops at a time, the Acid solution from the burette to the Alkali in the beaker: effervescence takes place, owing to the liberation of Carbonic acid gas, and the Alkali is gradually neutralized, according to the equation



After a time the Carbonic acid produced begins to change the colour of the litmus, and would mask the turning point of the reaction: this must be obviated by boiling the solution, when the Carbonic acid gas is driven off and the litmus is restored to its original blue colour. Keep on adding the acid gradually till the litmus is turned a red colour, which does not become blue on boiling. Note carefully the reading of the burette; this forms a rough indication of the amount of acid required.

For this rough determination methyl orange may be used as an indicator instead of litmus, and in that case no boiling is necessary, as its colour is not changed by the Carbonic acid liberated. Its use for accurate determinations should be avoided, as it is not so reliable in its results as litmus, and the turning point of the reaction is not so readily seen.

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After making the rough determination in the manner described above, the beaker should be rinsed out with distilled water, and the operation repeated with 10 c.c. of the N. Na_2CO_3 solution, this time proceeding very carefully when near the turning point, so that one drop of acid added turns the colour of the litmus. A third careful titration of 10 c.c. of N. Na_2CO_3 is next made, and the last two results should agree exactly.

Suppose 7.3 c.c. of the acid solution have been added in order to neutralize 10 c.c. of Normal Na_2CO_3 solution; clearly the acid solution has $\frac{10}{7.3}$ times the neutralizing power of the alkali. But the alkali is of Normal strength. Hence the acid is $\frac{10}{7.3}$ times Normal strength.

Now N. HCl contains 36.5 grams of Hydrochloric acid per litre of solution. Therefore the given solution of Hydrochloric acid must contain $\frac{10}{7.3} \times 36.5 = 50$ grams of Hydrochloric acid per litre.

If the Hydrochloric acid solution used in this experiment is stronger than the N. Na_2CO_3 —that is, if less acid than alkali was needed for the titration—it is quite simple to make up N. HCl from it; but if not, a stronger acid solution must be made up, and its strength ascertained as in the last experiment. Now, since Normal solutions contain equivalent quantities of acid Hydrogen and metal per litre, it follows that they neutralize one another in equal quantities by volume, that is, 10 c.c. of N. Na_2CO_3 neutralize 10 c.c. of N. HCl. Hence it follows that if the HCl solution of the last experiment is used, 7.3 c.c. of it must be diluted to 10 c.c. to make it exactly equivalent, bulk for bulk, to the N. Na_2CO_3 . So, in order to prepare 500 c.c. of the N. HCl, measure out carefully in a measuring-glass 365 c.c. of the HCl solution, place it all in a 500 c.c. flask, rinse out the measuring-glass with distilled water, pouring the rinsings into the flask, and fill up to the mark with distilled water. Shake up vigorously, and this solution should be N. HCl.

Test this by titrating 10 c.c. of the N. Na_2CO_3 with it, when exactly 10 c.c. of the HCl solution should be required.

To find the Strength of a Solution of Sulphuric Acid by comparing it with N. HCl and to make N. H_2SO_4 . First make up a solution of Caustic Soda by dissolving about half a stick of the solid in 100 c.c. of distilled water. Use this solution as the alkali and make accurate titrations with 10 c.c. of it against each of the acids separately, as in the last experiment. Litmus can be used as an indicator, but boiling is usually required, as Carbonic acid is nearly always present. Suppose 12.5 c.c. of the Sulphuric acid solution were required, and 15.4 c.c. of the N. HCl solution. Clearly the strength of the Sulphuric acid is $\frac{15.4}{12.5} \times \text{Normal}$, and since N. H_2SO_4 contains 49 grams of Sulphuric acid per litre, the strength of the given solution must be $\frac{15.4}{12.5} \times 49 = 60.37$ grams per litre.

In order to make N. H_2SO_4 from this solution, it is clear that 49 grams of Sulphuric acid are contained in $\frac{49}{60.37} \times 1000 = 811.6$ of the solution; so that if 811.6 c.c. of this solution are poured into a clean litre flask and the rest of the flask filled with distilled water, the litre flask will contain exactly 49 grams of Sulphuric acid, and the solution will be N. H_2SO_4 .

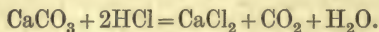
To prepare N. KOH. Make up about 500 c.c. of a fairly strong solution of Caustic Potash, and find its strength by titrating it against either of the Normal acid solutions already prepared. N. KOH contains 56 grams of Caustic Potash per litre, so, by calculating the quantity of the solution which contains the necessary weight of Caustic Potash, a 250 or 500 c.c. flask of N. KOH can be made up in a similar manner to the Normal acid solutions already prepared. Test this solution against the Normal acids; they should neutralize one another in exactly equal quantities.

To find the Equivalent Weight of Potassium Carbonate. Dry some Potassium Carbonate by heating it in a porcelain

dish and weigh out exactly 10 grams of it. Dissolve this in distilled water and make up the solution to 250 c.c.

Titrate this solution against Normal acid, and from the result of your experiments calculate the *weight* of Potassium Carbonate which will exactly neutralize 1000 c.c. of the Normal acid. This weight is the equivalent weight of Potassium Carbonate.

To find the Equivalent Weight of Calcium Carbonate. As this solid is insoluble in water, the method of the last experiment is not applicable. To determine its equivalent weight, weigh out into a beaker 1 gram of the dried Calcium Carbonate, and add to it 25 c.c. of N. HCl. This will dissolve the whole of the solid, and part of the acid will be neutralized according to the equation



Next, place some N. KOH in a burette and add it gradually to the acid mixture in the beaker, using litmus as an indicator, thereby ascertaining how much of the 25 c.c. of N. HCl is still unneutralized. From this the quantity needed to neutralize 1 gram of Calcium Carbonate can be deduced and the equivalent weight of this substance calculated.

To make this a little clearer, suppose n c.c. of N. KOH were necessary to complete the neutralization of the acid, then $25 - n$ c.c. of N. HCl must have been neutralized by 1 gram of Calcium Carbonate. Hence 1000 c.c. of N. HCl would neutralize $\frac{1000}{25 - n} \times 1$ grams of Calcium Carbonate, and this number is therefore its equivalent weight.

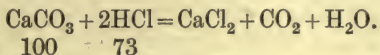
The equivalent weights of Barium, Strontium and Magnesium Carbonates can also be determined by this method.

To find the strength of a Solution of Hydrochloric Acid, using Iceland Spar. This is a very simple but rather tedious method for determining the strength of a solution of Hydrochloric acid.

A lump of Iceland Spar, about 5 to 10 grams in weight, is carefully weighed out; it is then placed in a beaker containing 25 c.c. of the given acid solution. Effervescence takes place, and the acid is gradually "killed" or neutralized by the

Calcium Carbonate. When no more effervescence occurs, even on warming, take out the lump of Spar, dry it with filter paper, and weigh it again carefully. Note its loss in weight.

The equation is



It is seen that 100 grams of Chalk neutralize 73 grams of HCl. Therefore for every gram of Iceland Spar dissolved .73 gram of HCl must have been present; hence the strength of the acid solution can be readily ascertained. The strength of a Nitric acid solution may also be determined by this method.

CHAPTER VI.

HYDROGEN.

Symbol, H. Atomic Weight, 1.008. Molecular Weight, 2.016.

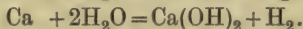
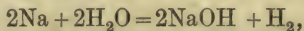
History. Paracelsus, in the sixteenth century, knew that a gas was evolved when Iron was placed in dilute Sulphuric acid, but Hydrogen was probably known some time before.

Up to the end of the eighteenth century, Hydrogen was classed with other combustible gases, such as Carbon Monoxide, Sulphuretted Hydrogen and the Hydrocarbons as "Inflammable Air."

Cavendish, about 1768, first ascertained its distinctive properties, but it was left to Lavoisier in 1783 to give it the name of Hydrogen.

Occurrence. Hydrogen is found in great quantities in nature. Water contains one-ninth of its weight of it; a very small fraction of the atmosphere consists of Hydrogen; all the oils and vegetable and animal matter in general contain it, whilst it is an essential constituent of all Acids.

Preparation. (1) *From Water.* Many metals will combine with the Oxygen in water, liberating all or part of the Hydrogen. Sodium, Potassium and Calcium, for instance, will liberate Hydrogen when placed in water, forming their respective Hydroxides, which latter cause the water to redden blue Litmus.



The liberation of Hydrogen from water by means of Sodium is best shewn by placing a glass tube 10 cm. long by 1 cm.

diameter, open at both ends, with its lower end just immersed in water (Fig. 16). Then, if a piece of Sodium metal as large as a pea is dropped into the tube, the evolved Hydrogen can be lighted as it escapes at the top. When Potassium is placed

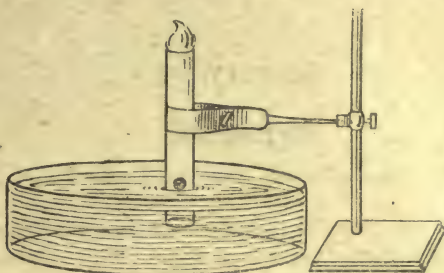
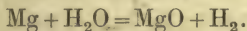


FIG. 16.—Action of Sodium on Water.

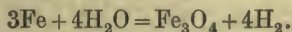
on water, the heat of the chemical action is sufficient to ignite the evolved Hydrogen, which burns with a lilac coloured flame, this colour being caused by the Potassium vapour.

Other metals, such as Magnesium, Zinc or Iron, will liberate the Hydrogen from steam, if it is passed over them when they are strongly heated.

The experiment with Magnesium is a striking one. Water boiled in the flask *A* (Fig. 17) causes steam to pass over a small quantity of Magnesium turnings contained in the test tube *B*, which has a small hole *C* blown through its end. On heating the Magnesium, it catches fire and burns brilliantly in the steam, and the evolved Hydrogen can be lighted as it issues from *C*. A white powder, Magnesium Oxide, is left in the test tube at the end of the experiment.



When steam is passed over Iron filings heated to redness in a furnace, Hydrogen gas is liberated very readily and the black magnetic Oxide of Iron is formed.



Hydrogen, as well as Oxygen, may be obtained from water

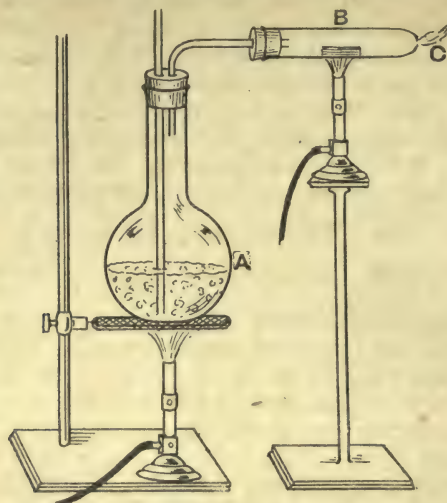


FIG. 17.—Action of Magnesium on Steam.

by passing a strong electric current through the water; the current is led into the water by means of two Platinum poles.

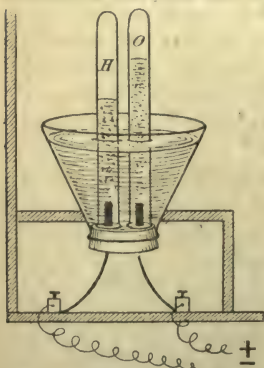


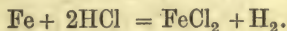
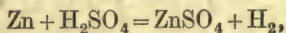
FIG. 18.—Electrolysis of Water.

Oxygen is evolved at the pole where the current enters the water (the + pole), and Hydrogen at the pole where the current leaves the water (the - pole). The volume of the Hydrogen evolved is a little more than double that of the Oxygen; it would be exactly double were it not for the fact that Oxygen is a little more soluble in water than Hydrogen. The process is called Electrolysis of Water.

If the water is quite pure, a very large pressure of electricity,

several thousand volts, must be employed, and even then the action proceeds slowly, but, by adding a little Sulphuric acid to the water, a pressure of only three volts suffices, and the action proceeds much more rapidly. A convenient form of apparatus is shewn in the diagram (Fig. 18).

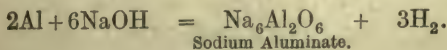
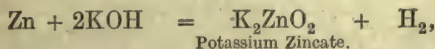
(2) *From Acids.* Most Acids yield Hydrogen gas when they act upon Magnesium powder. For practical purposes dilute Hydrochloric or Sulphuric acids are the best to use, and as metals, Zinc and Iron are the cheapest and most satisfactory.



The Hydrogen evolved from these reactions is by no means pure, owing to the impurities usually contained both in the metals themselves and the acids. For instance, the Hydrogen evolved by means of Iron always has an objectionable smell, due to Hydrocarbons formed with the Carbon which is always present in Iron.

That evolved from Zinc and Sulphuric acid is more pure, but never quite so; it contains Sulphuretted Hydrogen, due to the presence of Sulphur in the Zinc or to the reduction of the Sulphuric acid by nascent Hydrogen, Arseniuretted Hydrogen, due to the presence of Arsenic in the Zinc, or the acid, and several other impurities. The methods used for eliminating the impurities are seen in Dumas' experiment (p. 72). The purer the Zinc, the purer but the more slowly is the Hydrogen evolved; it is claimed that absolutely pure Zinc and Sulphuric acid diluted with pure water have no action upon one another.

(3) *From Alkalies.* Solutions of the Alkalies Caustic Potash and Soda, when warmed with the metals Zinc or Aluminium, will evolve Hydrogen gas very readily, the Zincates and Aluminates of Potash and Soda being formed.



From the reaction of water with the metal Potassium it is seen that this metal is capable of displacing only part of the Hydrogen from water, but if the resultant product, Caustic Potash, is heated with metallic Zinc, more Hydrogen is evolved from it. This indicates the presence of two portions of Hydrogen in water.

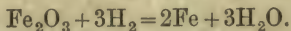
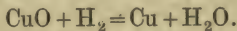
Properties. Hydrogen is a colourless, odourless gas, and is the lightest known substance. One litre of Hydrogen, under a pressure of 760 mm. of Mercury, and at a temperature of 0° C. (these are the standard conditions of pressure and temperature), weighs .0899 gram. Under the same condition 1 litre of Air weighs 1.2934 grams, so that the lifting power of Hydrogen per litre is 1.2035 grams; hence its great value as a material for filling balloons.

It is not a poisonous gas, but is quite incapable of supporting life. It is soluble only to a very slight extent in water, 100 c.c. of water dissolving 2.15 c.c. of the gas at 0° C.

Hydrogen gas is condensed to a colourless liquid at a temperature of -252° C.; this liquid has a density of .07, and is therefore extremely light; at a lower temperature it forms a white crystalline solid which melts at -258° C. The fact that liquid and solid Hydrogen are by no means metallic looking effectually disposes of the theory, once held, that Hydrogen is a metal.

Hydrogen combines very readily with Oxygen, and the flame produced by their union is one of the hottest known flames; when such a flame is caused to play upon a piece of infusible earth, such as Lime or Zirconia, it raises it to such a temperature that an intense white light is emitted. This Oxy-Hydrogen flame, as it is called, is used for welding Iron, melting and soldering Platinum, and for many other purposes for which a high temperature is required.

Reduction and Oxidation. Owing to the great affinity which Hydrogen has for Oxygen, it will take the element away from some hot metallic Oxides when it is passed over them, leaving the metal, thus:



These processes are called *Reductions*.

The opposite process—that of turning a metal into its Oxide—is called an *Oxidation*.

Latterly, since the putting forward of the Ionic Hypothesis (p. 166), the use of the terms Oxidation and Reduction has been widened. It will be seen later that compounds which ionize possess two parts, one carrying a positive electric charge, called the electro-positive part and usually metallic, the other carries a negative electric charge, and is called the electro-negative part.

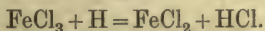
For example, in the compound Sodium Chloride (NaCl), Na is the electro-positive part and Cl the electro-negative; in Copper Sulphate (CuSO_4), Cu is electro-positive and SO_4 electro-negative.

Recognizing these definitions, the term Reduction is now applied to a reaction in which the proportion of the electro-positive part of a compound is increased, whilst Oxidation is a reaction in which the electro-negative part is increased. Thus a change from Ferrous Chloride FeCl_2 to Ferric Chloride FeCl_3 is spoken of as Oxidation, though Oxygen plays no part whatever in the reaction.

Similarly, a change from Mercuric Sulphate HgSO_4 to Mercurous Sulphate Hg_2SO_4 is known as a Reduction. Substances which will bring about Oxidation are known as Oxidizing Agents, whilst those which cause Reduction are called Reducing Agents.

On account of its action with metallic Oxides, mentioned above, Hydrogen is a powerful Reducing Agent.

Nascent Hydrogen. If bubbles of Hydrogen gas are passed through a solution of Ferric Chloride, nothing of moment occurs, but, if the Hydrogen is produced in the liquid itself by adding a little Hydrochloric acid and some Zinc dust, the yellow colour of the liquid is found to fade away, owing to the reduction of the Ferric Chloride to Ferrous Chloride, thus :



Hydrogen produced in this manner in a liquid is called *Nascent Hydrogen*, and is able to reduce many substances which are not reducible by gaseous Hydrogen. It is therefore

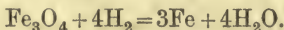
much used as a Reducing Agent, and one of the most important manufacturing processes—that of Aniline from Nitro-benzene—depends on Nascent Hydrogen for its working.

It is sometimes inconvenient to have an acid present in the liquid to be reduced by Nascent Hydrogen. This difficulty may be surmounted by using Aluminium powder and Caustic Potash to produce the gas. Thus the reduction of Saltpetre (KNO_3) to Ammonia gas may be affected by boiling with these two substances.

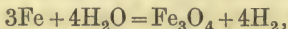


For a similar purpose Sodium amalgam may be used. This substance is made by rubbing, with a pestle, small pieces of Sodium into contact with a little Mercury contained in a mortar. This amalgam, when placed in water, evolves Hydrogen very slowly, leaving the water alkaline with Caustic Soda; the Mercury is unaffected.

Reversible Reactions. When Hydrogen gas is passed over red-hot magnetic Oxide of Iron contained in a tube, Reduction takes place, the Oxygen combines with the Hydrogen to form water and Iron is left, thus :

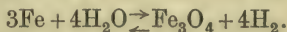


If this equation is compared with the one on page 57,

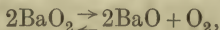


it is seen to be exactly the reverse of it.

Reactions of this type, which occur in both directions, as it were, are of common occurrence in Chemistry, and are called *Reversible Reactions*. “Reversed pointers” (\rightleftharpoons) are used instead of the symbol of equality (=) to denote this kind of action, to signify that the action may proceed from right to left or left to right, thus :



Another case of this nature was seen in the manufacture of Oxygen from Air when Barium Dioxide is used,



and many other instances will occur in due course. In each

instance, the conditions under which the reaction proceeds from left to right or *vice-versa* have been studied, and should be carefully noted.

For instance, in the case of Iron and Steam, mentioned above, the passing of a strong current of Steam over the Iron carries away the Hydrogen as fast as it is formed, and so prevents the opposing reaction occurring, and similarly the Hydrogen sweeps the Steam away in the other case.

But if some water is placed in a closed Iron vessel and heated to different temperatures, and the resultant gases at these temperatures are swept out quickly and analysed, it is found that, for each temperature, there is a definite proportion of Steam and Hydrogen present. For instance, at 200°C . the proportion of Steam to Hydrogen is 20 : 1, whilst at 440°C . it is only 6 : 1.

Clearly, then, under these conditions, an equilibrium is set up when the proportions of the two gases requisite for the given temperature is reached, which means that the two opposing reactions are proceeding at the same rate, exactly as much Hydrogen as Steam being liberated inside the vessel in a given time, so that the proportions do not change. To test this assertion, if an Iron tube is maintained at a temperature of 440°C ., and a mixture of Steam and Hydrogen in the proportion 6 : 1 is passed into it, the mixture which comes out at the other end of the tube is found to contain Steam and Hydrogen in exactly the same proportion, 6 : 1. This does not mean that no action has occurred, but that the opposing reactions have taken place inside the tube at exactly the same rate.

If the gases enter the tube in wrong proportions, it is found that, if passed slowly enough, the mixture at exit has the proper proportions for the temperature. The quantities of Iron and magnetic Oxide of Iron present have no effect on the action ; it is only the proportion in which the *gaseous* participants in the action are present which matters ; if a larger surface of Iron is presented to the action of the Steam, more of it may be turned into the Oxide, but an equivalent quantity of the Oxide will be reduced to Iron.

The Action of Hydrogen on Metals. Certain metals, particularly Palladium, Gold and Platinum, possess the power of absorbing large quantities of Hydrogen gas, especially when they are in a finely divided condition.

For instance, precipitated Palladium will absorb 500 times its volume, and spongy Platinum 50 times its volume of Hydrogen when heated for some time in the gas. When heated still more strongly, and especially if the pressure is reduced, the Hydrogen is evolved, and this furnishes a convenient method for getting small quantities of absolutely pure Hydrogen. The metals increase in volume during the absorption, though their general appearance and properties are unaltered, but, during the absorption, a considerable quantity of heat is evolved.

Thomas Graham (1868), who investigated this absorption of Hydrogen by Palladium very thoroughly, thought that the Hydrogen was condensed to a solid, to which he gave the name Hydrogenium to indicate its metallic nature. Solid Hydrogen, however, is much more like a non-metal than a metal, and its density is only one-eighth of that calculated for the absorbed Hydrogen in Palladium.



FIG. 19.—Diffusion.

Diffusion. If a jar of Hydrogen is placed above and mouth to mouth with a jar of Air (Fig. 19), though the Air is more than 14 times as heavy as the Hydrogen, it is found that, in a very short time, Hydrogen appears in the lower jar, and when a little time has elapsed, a mixture of the two is found in both jars.

Two liquids, which mix with one another, such as water and Alcohol, will, if the latter liquid is placed as a layer above the water, form a homogeneous liquid in a few days, but the time occupied is very much longer than in the case of gases.

This is because the molecules of gases possess a much higher degree of freedom than those of liquids; they are moving with a greater velocity, and the friction between the molecules is nothing like so great.

This motion of the molecules is, evidently, not an effect of gravitation, for the heavier gas or liquid moves upwards and the lighter downwards ; the process is called *Diffusion*.

Graham (1838) discovered that the rate at which gases diffuse is related to the density of the gas. He filled bottles, fitted with stoppers containing long tubes of narrow bore, with gases of different densities, and allowed the contents to diffuse into the air through the tubes for a given time. He then analysed the contents of the bottles and, from the results obtained, proceeded to propound what is now called "Graham's Law of Diffusion."

This states that *The relative speeds of diffusion of gases are inversely proportional to the Square Roots of the densities of the gases.*

Thus, comparing the four gases, Hydrogen, Oxygen, Methane and Carbonic acid gas :

	Density.	$\sqrt{\text{Density.}}$	Rate of Diffusion.
Hydrogen,	1	1	$\frac{1}{1} = 1$
Oxygen,	16	4	$\frac{1}{4} = \cdot 25$
Methane,	8	2.82	$\frac{1}{2.82} = \cdot 35$
Carbonic acid gas,	22	4.69	$\frac{1}{4.69} = \cdot 213$

This means that Hydrogen diffuses 4 times as rapidly as Oxygen, 2.82 times as rapidly as Methane and 4.69 times as rapidly as Carbonic acid gas.

The comparison of the rates of diffusion of other gases, with that of air, can be readily shewn by the apparatus in the diagram (Fig. 20).

A jar full of Hydrogen gas is placed round a porous pot made of unglazed earthenware, which is, of course, full of air to start with ; this pot is fitted with a cork, through which passes a long glass tube bent in the form of the letter U, and

having its lower half filled with coloured water to indicate the pressure. The molecules of Hydrogen enter the pot through the pores more rapidly than the molecules of air can escape; this produces an increase of pressure inside the pot, and the indicating liquid falls on the left-hand side.

With the other form of apparatus shewn in Fig. 20 the diffusion of the lighter air molecules out of the pot, which takes place more rapidly than the heavier Carbon Dioxide

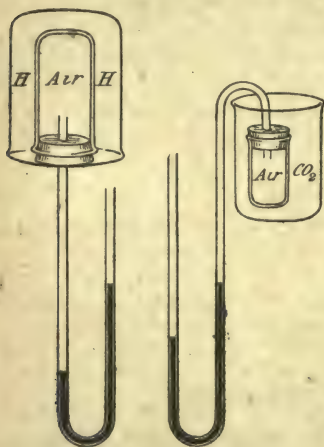


FIG. 20.—Diffusion of Gases.

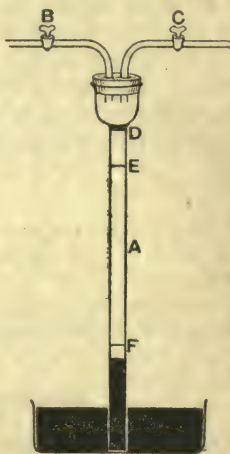


FIG. 21.—Comparison of Rates of Diffusion.

molecules can enter, causes a diminution of pressure, indicated by a rise of the liquid in the manometer towards the porous pot.

An apparatus for comparing roughly the rates of diffusion of different gases is shewn in the diagram (Fig. 21). The tube *A* is about half a centimetre in diameter and 80 cm. long; it has, sealed on to it, a wider piece of glass tubing in which a rubber cork is fitted. Through the cork pass two tubes with stop-cocks, and, at the point *D*, the tube is closed with a plug of some porous material such as Plaster of Paris.

The lower end of the tube is placed in a basin of Mercury, and, by means of a strong air-pump attached to the tube *B*, a fairly complete vacuum is made inside the tube, and the Mercury rises above the upper of the two marks, *E* and *F*, scratched on the tube.

The stop-cock in *B* is now closed and the other tube *C* is connected with a large jar full of the gas, whose rate of diffusion is to be tested. The stop-cock in *C* is fully opened, and the time taken by the Mercury to fall from the upper mark to the lower one is noted by a stop-watch.

The experiment is then repeated with other gases, and it is clear that the rates of diffusion of the different gases are inversely proportional, in each case, to the times taken by the Mercury to fall through the distance between the two marks.

PROBLEMS.

11. What weights of Iron and of Sulphuric acid will produce sufficient Hydrogen gas to fill a balloon of 12,000 litres capacity (1) at 0° C. and 760 mm. pressure, (2) at 15° C. and 750 mm. pressure?

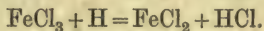
12. Determine the lifting power, at 0° C. and 760 mm. pressure, of a balloon of 50,000 litres capacity filled with Hydrogen gas.

PRACTICAL EXERCISES.

To reduce Metallic Oxides to the Metal by means of Hydrogen Gas. A very simple and effective method for obtaining specimens of some of the metals from their Oxides consists in placing two or three grams of the Oxide in a piece of hard glass tubing about 20 cm. long, passing Hydrogen gas through the tube, and then heating it with a bunsen burner. Care must be taken not to heat the tube till the Hydrogen gas has been passed through it for some time, or an explosion may occur through the presence of Air in the Hydrogen generating flask. Oxides of Copper, Lead, Iron, Nickel or Tin may be reduced in this way.

To reduce Ferric Compounds to Ferrous Compounds by means of Nascent Hydrogen. Take about 25 c.c. of a solution of Ferric Chloride in a boiling tube, add 5 c.c. of strong Hydrochloric

acid and a few grams of granulated Zinc. As the Hydrogen is evolved the yellow colour of the solution gradually fades, shewing that the Ferric Chloride is being reduced to Ferrous Chloride.



To prove that reduction has taken place, add to the original Ferric Chloride some Potassium Sulphocyanide solution, when a blood-red coloration is produced, but the reduced solution shews no trace of colour with that reagent.

Again, add to both solutions some Potassium Ferrieyanide ; with the Ferric Chloride a brown coloration appears, but with the reduced solution there is formed a dark-blue precipitate.

To reduce Potassium Nitrate to Ammonia by Nascent Hydrogen. Take a gram or two of Potassium Nitrate in a boiling tube, add to it some Caustic Soda solution and a little Aluminium powder. Warm gently and Ammonia gas is formed by reduction, and may be recognized by its smell and the fact that it turns red litmus paper blue.

This method of forming Hydrogen is used in this experiment, because, if an acid were used, the Ammonia gas would combine with the acid and would not be evolved.

To compare the Rates of Diffusion of Coal Gas and Air. This may be done, roughly, by an experiment similar to the one described on p. 66 (Fig. 21). The times for the diffusion of Coal gas and Air should be

$$\sqrt{8} : \sqrt{14.4} ; \text{ i.e. } 1 : 1.34.$$

CHAPTER VII.

WATER.

Formula, H_2O . Molecular Weight, 18.016.

Occurrence. Water, in its three states of ice (or snow), water and steam (or water vapour), is very widely distributed in nature, and it is estimated that about 75 per cent. of the matter on the earth's surface consists of water.

Living organisms contain water in large quantities, *e.g.* the human body contains 70 per cent., plants between 50 and 80 per cent.; it is also found combined or absorbed in rocks; clay, for instance, contains about 14 per cent. of combined water.

How to recognize Water. It has been solemnly stated that no one has ever seen pure water, and this statement is probably correct, for, owing to its great power of dissolving other substances, the moment it comes into contact with any kind of matter, whether solid, liquid or gaseous, it dissolves some of it and is no longer pure.

By boiling impure water and condensing the steam, *distilled water*, as it is called, is obtained, and this contains few solid impurities, and is purest when the condenser is made of Tin, which is far less soluble than glass. Organic impurities distil over with the steam, but these may be stopped by adding a little Potassium Permanganate solution to the water before distilling. Distilled water may be recognized by the following properties:

- (1) It has no colour in small quantities and is odourless.
- (2) It has no effect on either red or blue litmus.

- (3) It leaves no residue on evaporation.
- (4) It freezes at 0°C . and boils at 100°C ., when the barometric pressure is 760 mm.
- (5) Its density at 4°C . is 1 ; i.e. 1 c.c. of it weighs 1 gram.
- (6) It turns white anhydrous Copper Sulphate blue.

This last test will shew the presence of water, even if it is very impure.

Composition. The composition of any compound body may be ascertained in two ways: (1) By splitting it up into its parts ; this process is called *Analysis* ; (2) by building it up from its parts ; this is called *Synthesis*.

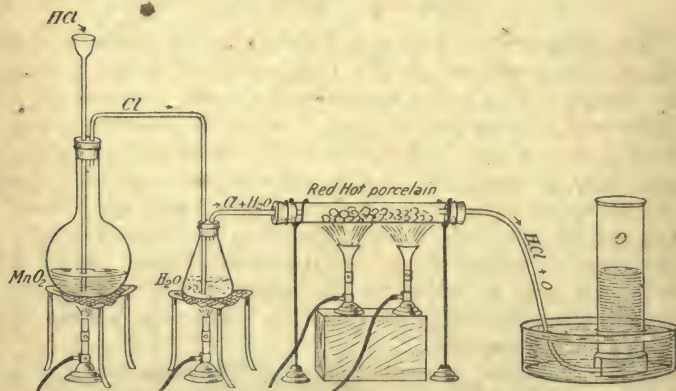


FIG. 22.—Preparation of Oxygen from Water.

Water was, for a long time, considered to be an elementary substance, till Cavendish, at the end of the eighteenth century, shewed that, when a mixture of two volumes of Hydrogen and one volume of Oxygen were exploded together in a perfectly dry vessel, water was produced.

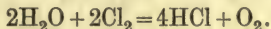
Analysis of Water. It has already been seen that when water, or steam, acts upon the metals Sodium or Magnesium, Hydrogen is produced.

This must have come from the water, since both the metals are elementary substances.

The presence of Oxygen in water can be shewn by the following experiment: Chlorine gas is made by warming a mixture of Manganese Dioxide and Hydrochloric acid (Fig. 22); it is bubbled through boiling water contained in a flask, and the mixture of Chlorine and Steam is passed through a red-hot porcelain tube containing pieces of broken porcelain. The resulting products of the action are led into water, and Oxygen gas is found to collect in the receiver.

This must have come from the water, since Chlorine is elementary, and the porcelain is unaffected.

In this experiment Hydrochloric acid gas is also formed, thus :



The Hydrochloric acid gas dissolves in the water in the basin. The porcelain acts as a Catalytic agent, probably only by offering a large heated surface to the action of the gases.

By these analytical experiments it is seen that water contains both Hydrogen and Oxygen, but it must be clearly recognized that they do not prove that it contains nothing else. The electrolysis of water (p. 58) definitely proves this, for Hydrogen and Oxygen are evolved and nothing but water is left in the vessel in which the electrolysis is conducted. Even if Sulphuric acid is added to the water before electrolysis, exactly the same weight of the acid is found to be present at the end of the operation.

Since, moreover, the proportions of Hydrogen to Oxygen formed during electrolysis are approximately as 2 is to 1, it follows that the proportion of Hydrogen, by volume, in water is double that of Oxygen, but this fact is more satisfactorily proved by Synthesis.

Synthesis of Water. If some Copper filings are heated in a stream of pure Oxygen, they turn black and increase in weight. Clearly they have absorbed some of the Oxygen, and the black substance formed must contain Copper and Oxygen only; it is called Copper Oxide.

If, now, some of this black Copper Oxide is placed in a hard glass tube (Fig. 23), heated, and dry Hydrogen gas passed over it, a liquid collects in the cooled U-tube attached

to the apparatus, which answers all the tests for water. On examining the hard glass tube, its contents are found to be pure Copper.

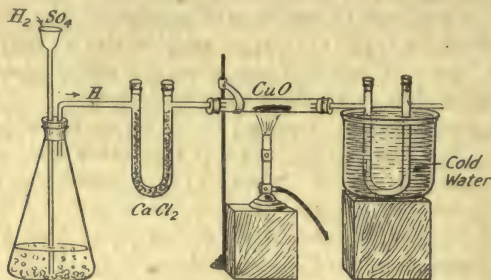


FIG. 23.—Composition of Water by Synthesis.

Since Hydrogen was admitted to the tube, this is a convincing proof that water contains Hydrogen and Oxygen only.

This simple experiment was the basis of a much more elaborate series of experiments conducted by Dumas (1842), by which the accurate composition of water by weight was determined.

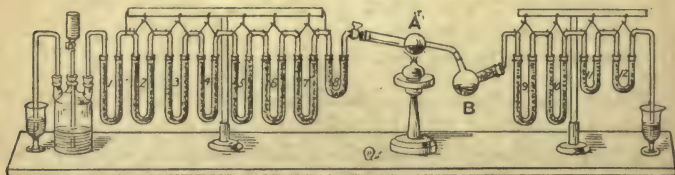


FIG. 24.—Dumas' Experiment.

He prepared Hydrogen by acting upon Zinc with dilute Sulphuric acid, and purified it very completely by passing it through a series of U-tubes each one metre high (Fig. 24).

No. 1 contained pieces of glass moistened with a solution of Lead Nitrate to absorb Sulphuretted Hydrogen.

No. 2 was a similar tube containing Silver Sulphate to absorb Arseniuretted Hydrogen and Phosphoretted Hydrogen.

Nos. 3, 4 and 5 contained solid Caustic Potash to absorb Sulphur Dioxide, Carbon Dioxide and part of the water vapour.

Nos. 6 and 7 contained Phosphorus Pentoxide to absorb the rest of the water, and were immersed in a freezing mixture.

No. 8 contained Phosphorus Pentoxide. This tube was weighed before and after the experiment to test if the Hydrogen was quite dry; if any increase in weight was observed in it, the results of that experiment were discarded.

The purified Hydrogen passed over Copper Oxide heated to redness in the bulb *A*, and most of the water was condensed in the succeeding bulb *B*. The rest of the water was absorbed by solid Caustic Potash in the U-tube No. 9, and by Phosphorus Pentoxide in the U-tubes Nos. 10 and 11, these two being kept cold by immersion in a freezing mixture.

No. 12 contained Phosphorus Pentoxide placed there to prevent any access of water vapour from the air to the other U-tubes.

The weight of Oxygen was obtained from the loss of weight in the bulb tube *A* containing the Copper Oxide, and the weight of water from the increase of weight in the bulb *B* and the U-tubes 9, 10 and 11.

The average of nineteen experiments by Dumas gave :

Loss of weight of Copper Oxide	-	44.22	grams.
Gain in weight due to water	-	49.76	„
Weight of Hydrogen (by difference)	-	5.54	„

From these figures it is found that 2 parts by weight of Hydrogen combine with 15.96 parts of Oxygen.

A later and very accurate determination of the composition of water by weight is due to Morley (1895).

The apparatus used was that shewn in the diagram (Fig. 25). This was made quite vacuum and weighed, then pure dry Oxygen and Hydrogen were admitted through the tubes *A* and *B* from glass globes which had been previously weighed. The gases were caused to combine by electric sparks passing continuously between the terminals at *C*. As the water formed by the union condensed, a fresh vacuum was formed, and more of the gases were admitted and caused to unite.

Eventually the influx of gases was stopped, the apparatus weighed, exhausted of its contents (whose composition was ascertained), and weighed again.

The increase in weight gave the weight of the water formed, and the decrease in weight of the glass globes which contained the Oxygen and Hydrogen, less, in one case, the weight of the

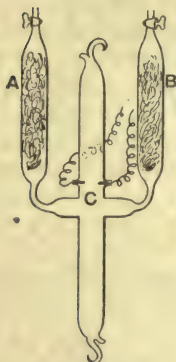


FIG. 25.—Morley's Experiment.

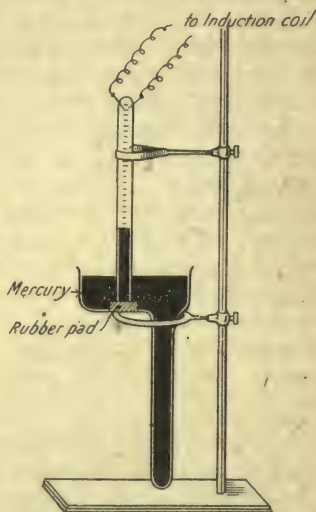


FIG. 26.—Eudiometric Synthesis of Water.

residual gas in the apparatus, gave the weights of the combining gases.

To prevent loss of water vapour the tubes *A* and *B* contained Phosphorus Pentoxide.

With this apparatus Morley found that 16 parts by weight of Oxygen combined with 2.015 parts of Hydrogen.

Eudiometric Synthesis of Water. Cavendish's experiment on the synthesis of water by volume, may be repeated with the more modern form of the apparatus shewn in the diagram (Fig. 26).

This consists of a long graduated tube of stout glass, closed at one end and having two Platinum wires passed through the glass near the closed end, their ends not quite touching inside the tube. This tube is called an *Eudiometer*.

It is filled with Mercury and inverted in a trough also containing Mercury.

Pure dry Oxygen gas is passed in, the levels of Mercury inside and outside the tube are made equal by lowering it into the lower part of the trough, and its volume measured.

More than twice this volume of pure dry Hydrogen is then passed in and its volume ascertained after levelling as before.

The open end of the tube is then pressed down on a rubber pad and the mixture fired by causing a spark to pass between the Platinum wires. The contents are then allowed to cool to the temperature of their surroundings, and the volume of the resultant gas—Hydrogen—is read after levelling as before.

Since the temperature and pressure have remained constant throughout the experiment, it will not be necessary to make any corrections of the observed volumes.

The exact volume composition of water can be calculated as follows :

Volume of Oxygen	- - - - -	22.4 c.c.
Volume after adding Hydrogen	- -	127.3 c.c.
Whence volume of Hydrogen present at beginning	- - - - -	104.9 c.c.
Volume of Hydrogen after explosion	-	60.1 c.c.

Whence 22.4 c.c. of Oxygen have combined with 44.8 c.c. of Hydrogen, and these numbers are exactly in the proportion of 1 : 2.

It will be proved later that the molecules of both Hydrogen and Oxygen gases each contain two atoms, and may be represented by the formulae H_2 and O_2 .

Using this fact, if Avogadro's Hypothesis is accepted, namely, that equal volumes of all gases, under the same conditions of temperature and pressure, contain an equal number of molecules, it follows, from the experiment described above, that 2 molecules of Hydrogen combine with 1 molecule of

Accepting Avogadro's Hypothesis, it follows that 2 molecules of Hydrogen and 1 molecule of Oxygen produce 2 molecules of Steam; in other words, 1 molecule of Steam contains 1 molecule of Hydrogen (H_2) and half a molecule of Oxygen (O), and hence its formula must be written H_2O .

Gas Analysis. The fact that 2 volumes of Hydrogen and 1 volume of Oxygen unite, if ignited, to form water, whose volume is so small that it may be neglected, is made use of in the analysis of gaseous mixtures containing either of these gases. A large excess of the other gas is added, the mixture sparked and the diminution of volume carefully noted.

Since the diminution consists of Hydrogen and Oxygen in the proportion 2 : 1, two-thirds of it must consist of Hydrogen and one-third of Oxygen, and hence the volume of either gas present in the original mixture can be found. An example will make this clear in the case of Air.

Volume of Air taken	-	-	-	27.2 c.c.
Volume after adding Hydrogen	-	-	-	55.4 c.c.
Volume after explosion	-	-	-	38.3 c.c.

The contraction is 17.1 c.c., of which one-third, *i.e.* 5.7 c.c., must be Oxygen.

$$\text{Hence percentage of Oxygen in Air} = \frac{5.7}{27.2} \times 100 = 20.9.$$

The Properties of Water. At ordinary temperatures pure water is a tasteless and odourless liquid. In small quantities it is colourless, but, when a thick layer of it is seen, it possesses a greenish colour.

The presence of very finely divided solid matter suspended in water gives to it a blue colour; this is seen in china clay settling pits and also in many Swiss lakes into which fine glacial mud is carried by streams.

Water, like all liquids, is only slightly compressible. 1 litre of water is compressed .05 c.c. by a pressure of 2 atmospheres; slight though this compression is, it has been calculated by P. G. Tait that, were it not to take place, the sea-level would be more than 100 feet higher than is at present the case.

Water boils at 100°C . under a pressure of 760 mm. of Mercury ; the boiling point is higher under increased pressure and lower for diminished pressure ; this alteration of boiling point is common to all liquids, and the pressure must therefore always be stated when the boiling point of a liquid is given.

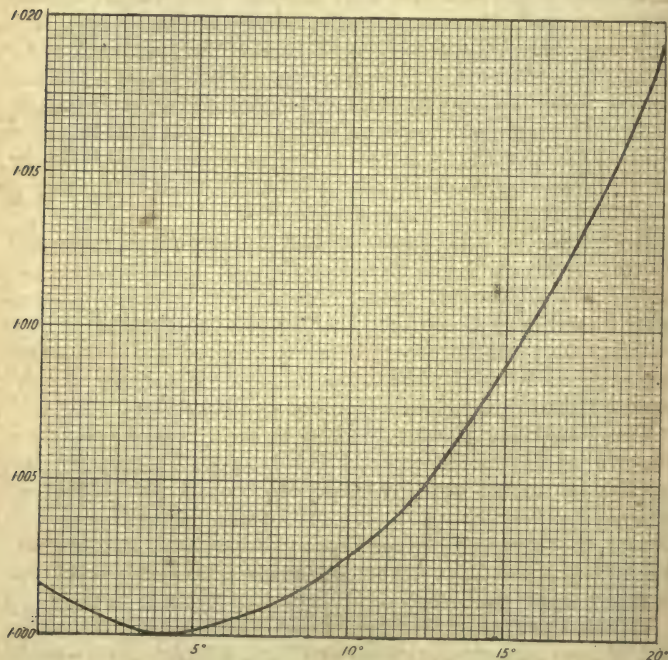


FIG. 28.—Maximum Density of Water.

Liquid water freezes at 0°C . to crystalline ice, and, at the same temperature, water vapour forms the very small, but complex, crystals of hoar-frost and snow. When water at 0°C . is heated gradually it does not follow the general rule of expansion under heat, for, up to a temperature of 4°C ., it contracts, and not till it gets above that temperature does it begin to expand.

This peculiar behaviour of water is shewn in the diagram (Fig. 28), which gives, by means of a graph, the relation between the volume and the temperature of a given mass of water from 0° C. to 20° C.

From this graph it is seen that water has its maximum density at a temperature of 4° C., and this fact has a most important and interesting result on water in Nature.

When a mass of water is cooled, from 10° C. say, by the cold atmosphere above it, the cooled water is denser than the uncooled water and sinks, while the warmer water takes its place. This circulation goes on till the whole mass of the water is at 4° C., then the cooler water is less dense than the water at 4° C. and remains at the surface, ultimately forming a coating of ice which is less dense still.

Since both ice and water are bad conductors of heat, this coating of ice does not attain any great thickness, and the water at no great depth is, and remains at 4° C., a temperature quite bearable by fishes and other forms of aquatic life.

When changing into ice, water expands; 100 c.c. of water becoming approximately 110 c.c. of ice, which latter is consequently less dense than water and floats on it.

This expansion during freezing is most important in its effects; it bursts the intercellular tissues of plants by the freezing of the cell sap; it causes the cracking and breaking of rocks by the freezing of the water contained in their interstices: this breaking becomes apparent during a 'thaw,' when the broken pieces fall away and collect as a talus at the bottom of rocky slopes and cliffs.

Vapour Pressure of Water. As has been seen in the process of Diffusion, the molecules of water are in more or less rapid motion, but, as they are, in all probability, much more closely packed than the molecules of gases, they are more under the influence of comparatively powerful inter-molecular forces.

When a molecule of water approaches the surface, if its velocity is great enough to take it beyond the range of these inter-molecular forces, it will escape into the surrounding atmosphere, but, if not, it will only rise a short distance, and

then the molecular attraction will drag it back into the liquid again. This behaviour is shewn diagrammatically in Fig. 29 ; it is analogous to the behaviour of a projectile shot away from the earth's surface, with a velocity sufficiently great to carry it beyond the bounds of the earth's gravitational attraction, so that it never returns to the earth again.

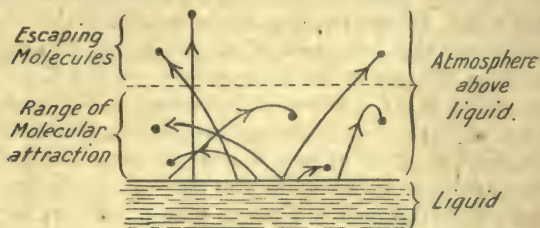


FIG. 29.—Evaporation of Water.

A rise in temperature produces an increase in the velocity of the molecules and, consequently, a greater number escape ; the process is called *Evaporation*.

When a liquid is evaporating into a closed vacuous space, the escaping molecules cannot get right away, and so accumulate in the space above the liquid, and their concentration in the space will go on increasing and, as they are still in motion, a certain percentage will plunge back into the liquid.

When the number of molecules which return to the liquid in a given time is equal to the number of molecules which escape from the liquid in the same time, equilibrium is established, and the vapour is said to be *saturated*.

Experiments have established the fact that the vapour pressure of a liquid is a constant quantity, and depends only on the temperature, and is independent of the quantity of liquid or vapour present.

Dalton shewed that the vapour pressure of a liquid at a given temperature is the same whether the liquid is by itself or associated with other vapours or gases upon which it has no chemical action.

In other words, the total pressure of a mixture of gases and

vapours is the sum of the partial pressures of each constituent of the mixture.

This is made use of in the determination of the correct volume of a gas measured after being collected over water.

If the volume is measured at the pressure of the atmosphere, *i.e.* if the levels of water inside and outside the tube are the same, the true pressure of the gas alone is obtained, from Dalton's law, by subtracting the maximum vapour pressure of water at the temperature at which the observation is taken from the atmospheric pressure.

Example. What is the volume at standard temperature and pressure of 124 c.c. of Hydrogen gas measured over water at a temperature of 12° C. under a barometric pressure of 754 mm.?

The vapour pressure of water at 12° = 10.5 mm. (p. 492).

Hence the Hydrogen is under a partial pressure of

$$754 - 10.5 = 743.5 \text{ mm.}$$

The corrected volume required is therefore

$$124 \times \frac{743.5}{760} \times \frac{273}{285} = 115 \text{ c.c.}$$

PROBLEMS.

13. The results of an experiment, similar to that of Dumas, on the composition of water were :

Weight of Copper Oxide tube	before experiment,	31.79 grams.
" " "	after	" 26.21 "
" Phosphorus Pentoxide tubes	before	" 42.51 "
" " "	after	" 48.88 "

Calculate from these figures the percentage composition of water by weight.

14. 80 c.c. of a mixture of Oxygen and Nitrogen were exploded with 150 c.c. of Hydrogen. The volume after explosion was found to be 155 c.c. Calculate the percentage of Oxygen in the mixture.

PRACTICAL EXERCISES.

To determine the Composition of Water by Weight. Dumas' experiment may be repeated, with fair accuracy if great care
o.c.
F

is taken, by using an apparatus similar to the one in Fig. 23. To this must be added an extra U-tube for drying the Hydrogen gas, containing pumice stone soaked in strong Sulphuric acid, and another small U-tube containing Calcium Chloride joined on to the U-tube which is immersed in the water. These last two U-tubes must be weighed together before and after the experiment, and the increase gives the weight of water formed, whilst the decrease of the Copper Oxide tube gives the weight of the Oxygen contained in that water.

CHAPTER VIII.

SOLUTION AND CRYSTALLIZATION.

A **Solution** is a homogeneous mixture of a liquid and a gas, or a liquid and a solid. The liquid is called the *Solvent* and the gas or solid which is dissolved in it is called the *Solute*.

If two liquids mix together to form one homogeneous liquid, one of them may be said to dissolve in the other, but it is difficult to say which is the *Solvent* and which the *Solute*. Solutions are of two kinds—Physical and Chemical.

In a **Physical** solution the *Solute* is unaltered and may be obtained again by evaporation of the *Solvent*. Examples of this are, Sugar in Water and Sulphur in Carbon Disulphide.

In a **Chemical** solution the *Solute* is changed in the process and a different substance is obtained by evaporation. Examples are, Zinc in Sulphuric acid and Sodium in Water.

Water is one of the most active of *Solvents*; indeed it is stated that there is no substance, whether solid, liquid or gas, which does not dissolve to some extent in water.

Solution of Gases in Water. The quantity of gas dissolved by water depends upon three things : (1) the nature of the gas, (2) the temperature of the water, (3) the pressure.

(1) The variations under this head are very great. For instance, 100 c.c. of water at 0° C. will dissolve approximately 2 c.c. of Nitrogen, 4 c.c. of Oxygen, 180 c.c. of Carbonic acid gas and 114,800 c.c. of Ammonia.

(2) The effect of increase of temperature is to decrease the quantity of gas dissolved. The following table shews this

decrease in the amount dissolved by 100 c.c. of water for different gases :

Temperature.	Hydrogen.	Oxygen.	Carbon Dioxide.
0° C.	2.15	4.11	179.6
5° C.	2.06	3.62	144.9
10° C.	1.98	3.25	118.4
20° C.	1.84	2.83	90.1

The gas Helium, between the temperatures of 25° C. and 50° C., is believed to be an exception to this rule.

It follows that, if a saturated solution of a gas is heated, some of the gas is expelled, and, if the water is boiled for some time, the whole of the gas, in most cases, is driven off. One exception is Hydrochloric acid gas, a solution of which, when it attains a certain strength, distils over unchanged (p. 191).

(3) The effect of increase of pressure on the solubility of gases was discovered by Henry (1803), and is given by Henry's Law, which states that "*The volume of a gas absorbed by a liquid is directly proportional to the pressure of the gas, if the temperature remains constant.*"

This means that, if the pressure is doubled, the quantity of gas dissolved is doubled, and so on.

The result of this is well seen in the ordinary soda-water bottle, in which Carbonic acid gas is dissolved in water under increased pressure ; when the cork is drawn out the water can no longer dissolve the same amount of gas under the reduced pressure, and it therefore escapes in the form of bubbles.

Since, from Boyle's Law, the volume of any gas is inversely proportional to the pressure, Henry's Law may be stated thus : "A given volume of water will dissolve the same volume of a gas at all pressures."

Solubility of Liquids in Water. Liquids dissolve in water after two fashions : (1) when the liquid and water mix together in all proportions, (2) when only a portion of the liquid dissolves and the rest separates out.

An example of the first kind is seen in a mixture of Alcohol and Water, which mix together whatever the proportions in which each is present.

An example of the second type is seen when Ether and Water are mixed together ; after shaking, the liquid separates into two layers, the lower one consisting of Water with a little Ether dissolved in it, and the upper one of Ether with a little Water dissolved in it.

The presence of the Ether in the Water can be shewn by boiling the Water, when Ether vapour is evolved which will ignite, whilst the Water dissolved in the Ether can be detected by means of anhydrous Copper Sulphate.

Solution of Solids in Water. When a solid substance is immersed in Water the energy of the rapidly moving molecules of the Water tends to break down, to a greater or less extent, the attraction of the molecules of the solid for one another, and some of these solid molecules pass into, and through, the Water.

As these molecules move about through the Water, they sometimes return to the solid again and, when the number of those leaving and returning is equal, equilibrium is established, and the solution is said to be *Saturated* for that particular solid.

Since at higher temperatures the Water molecules are in more rapid motion, and their energy consequently greater, a hot saturated solution contains, in most cases, a larger amount of the solid than a cold one.

The **Solubility of a Solid** at any temperature is given usually as the number of grams of that solid dissolved by 100 grams of Water:

By determining this solubility (p. 92) for different temperatures, curves may be plotted shewing the relation between the solubility and the temperature, and a few of these are shewn in the diagram (Fig. 30).

A careful study of these curves reveals some interesting facts. For instance, the solubility of Sodium Chloride (common Salt) increases but little with rise of temperature, while that of Potassium Nitrate (Saltpetre) has an enormous increase.

The curve for Sodium Sulphate is, at first sight, anomalous ; its peculiar conformation is explained by the fact that this substance occurs in three distinct forms : (1) Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, which contains 10 molecules of Water of crystallization ; (2) $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, which only has 7 molecules

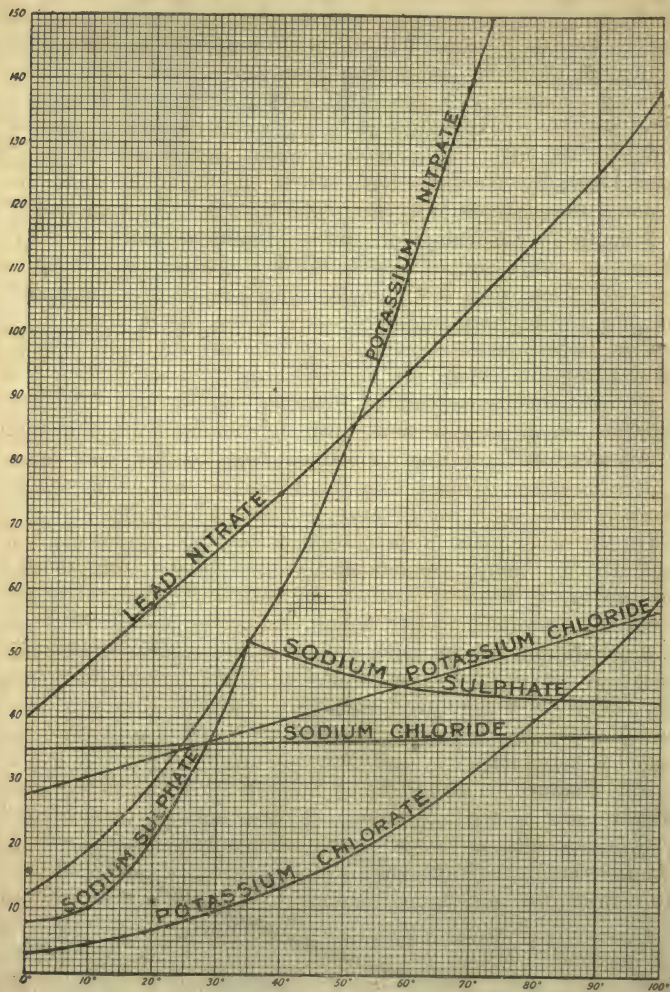


FIG. 30.—Curves of Solubility.

of Water of crystallization ; and (3) Na_2SO_4 , the anhydrous salt. The first portion of the curve represents the solubility of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; for example, at 30°C . the solution of this salt contains 39 grams of Na_2SO_4 in 100 grams of water. Now $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ melts at 34°C ., so, above that temperature, the anhydrous salt only can exist, and its solubility is represented by the second portion of the curve, in which it is noted that the solubility decreases with rise of temperature.

When a hot saturated solution is allowed to cool down, the Water, as a rule, cannot hold so much of the solid in solution ; part of it separates out, leaving the liquid still a saturated solution at the temperature to which it has fallen.

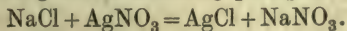
This indicates a good method of separating a mixture of two salts in solution when their solubilities differ.

For instance, a mixture of Potassic Chloride and Potassic Chlorate can be separated to a very great extent by allowing a hot saturated solution containing them both to cool ; the Chlorate separates out owing to its smaller solubility at low temperatures, while the Chloride remains still in solution.

On the other hand, a mixture of Salt and Saltpetre can be separated by boiling a hot saturated solution containing both, for, owing to its greater solubility at 100°C ., the Saltpetre remains in solution, whilst the Salt separates out.

Precipitation. Many salts, which are but sparingly soluble in Water, are of great value to the Analytical chemist, owing to the fact that, if they are formed *in* the liquid, they separate out from it because of their insolubility ; such a separation is called a *Precipitate*.

For instance, if solutions of Sodium Chloride and Silver Nitrate are mixed together, the sparingly soluble Silver Chloride is formed in the liquid and is precipitated. The reaction is shewn in the following equation, the sign of the downward pointing arrow denoting precipitation.



As many of the precipitates thus formed possess distinctive colours, they are readily recognized and indicate the presence of the Base (or the Acid) which they contain.

Supersaturation. Solutions of certain substances, notably Sodium Thiosulphate (the "Hypo" of the photographer), Sodium Acetate and Sodium Sulphate, can be obtained, which contain much more of the solute than is necessary to saturate them at the temperature of observation. This may be brought about by allowing hot saturated solutions to cool very slowly, taking care that none of the solute in solid form and no dust is present, or is allowed access to the liquid. Such a solution is said to be *Supersaturated*.

The condition in a supersaturated solution is an unstable one, for, if a crystal of the dissolved solid is introduced, the solute immediately separates out, and continues to do so till the strength of the solution is that required for saturation at the temperature of observation. At the same time, a considerable rise of temperature takes place, due to the Latent Heat evolved by the liquid solute changing into solid form.

Water of Crystallization. When a solid separates out from its cooling saturated solution, it usually does so, especially if the cooling proceeds slowly, in the form of crystals. For most solids there is a perfectly definite shape in which each crystallizes, and, though the size of the crystal faces may vary and the crystal look distorted, the angles between any two faces are invariable however distorted the crystal appears. A few ideal crystals are shewn in the diagram (Fig. 31).

Crystals of Salt, Saltpetre and several other substances are usually anhydrous, but the majority of crystals deposited from solution in Water contain Water, which is called *Water of Crystallization*.

For instance, Copper Sulphate crystals contain 5 molecules of Water for every molecule of Copper Sulphate, and its formula is written $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Similarly, that of Magnesium Sulphate (Epsom Salts) is $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and Crystalline Calcium Sulphate (Gypsum) is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Certain salts possess the power to crystallize with more than one number of molecules of Water, this number depending upon the temperature at which the crystallization takes place. For instance, Salt when crystallized at ordinary temperatures, about 15°C ., has no Water of crystallization, but, if

crystals are deposited from a solution at -7°C ., they contain 2 molecules of Water, $\text{NaCl} \cdot 2\text{H}_2\text{O}$, and if at -27°C . 10 molecules of Water are present, and the formula is $\text{NaCl} \cdot 10\text{H}_2\text{O}$.

Similarly with Sodium Carbonate (Washing Soda); from a solution at ordinary temperatures, crystals of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ are formed, but if the crystals are deposited from solutions between 30°C . and 50°C ., they contain less Water of crystallization and have a formula $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$.

Most of the Water which crystals contain is evolved when they are heated to a temperature of 100°C ., but in several



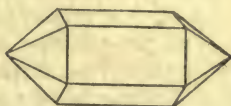
Salt Crystal (Cube).



Alum Crystal (Octohedron).



Potassium Chlorate Crystal.



Quartz Crystal (Hexagonal).

FIG. 31.—Ideal Crystals.

cases part of the Water is retained up to much higher temperatures.

For instance, Copper Sulphate crystals part with 4 out of the 5 molecules of Water which they contain, at 100°C ., but the fifth is not given off till the temperature is raised above 200°C .

Again, Zinc Sulphate crystals, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, lose 6 molecules of Water at 100°C ., but retain the seventh till a temperature of 240°C . is reached.

Certain crystalline salts lose all or part of their Water of crystallization at ordinary temperatures; for instance, Washing Soda crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, on exposure to the air, gradually

lose their crystalline form and become a white powder, which consists of tiny crystals of a different crystalline form and a formula $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

Such substances are said to *effloresce*, and the process is called *Efflorescence*.

With other substances the reverse process occurs, for, on exposure to air, they absorb Water, and either form crystals containing more molecules of Water of crystallization or absorb sufficient Water to dissolve in it and form a liquid.

They are said to *deliquesce*, and the process is called *Deliquescence*.

To the former class belongs $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, which absorbs 4 more molecules of Water, becoming ordinary blue vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

To the latter class belong the Chlorides of Calcium and Iron, CaCl_2 and FeCl_3 , which rapidly become liquid solutions when exposed to air.

The percentage of Water of Crystallization contained in a substance can be ascertained by keeping a weighed quantity of it contained in a crucible at a temperature of about 200°C . in a hot-air bath, and noting the resulting loss in weight.

If the formula of the salt is known, and the Atomic Weights of the elements contained in it, the number of molecules of Water of crystallization it contains can be calculated by a similar experiment.

Example. 431 gram of Zinc Sulphate crystals, $\text{ZnSO}_4 \cdot x\text{H}_2\text{O}$, left on heating for some time 241 gram of the anhydrous salt. Find x .

The molecular weight of $\text{ZnSO}_4 = 65 + 32 + 64 = 161$.

That of the crystals is therefore $161 + 18x$.

These numbers are clearly proportional to the two weights, 241 and 431, obtained in the experiment, *i.e.*

$$\frac{241}{161} = \frac{431}{161 + 18x};$$

whence $x = 7.05$, and the nearest whole number being 7, the formula is $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Isomorphism. Certain salts are noticed to crystallize in

precisely the same form, and when this occurs they are said to be *isomorphous*. Thus, the Sulphates of Zinc and Magnesium, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, form crystals which are identical in their shapes,

Mitscherlich (1821) put forward a Law of Isomorphism, in which he stated that "The same number of atoms, combined in the same way, give rise to the same crystalline form, which is independent of the nature of the atoms, being influenced only by their number and mode of arrangement."

If two soluble salts are isomorphous, a crystal of one of them will continue to grow when suspended in a saturated solution of the other. For instance, if a deep mauve crystal of Chrome Alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, is suspended in a saturated solution of Potash Alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, a colourless deposit of the latter salt is formed over the dark crystal of Chrome Alum. Such a phenomenon is known as an *Overgrowth*.

Again, if a saturated solution containing two isomorphous salts is allowed to crystallize, the crystals formed will be found to contain both salts, though in appearance they are quite homogeneous. Such crystals are called *Mixed Crystals*.

PROBLEM.

15. 59 gram of Magnesium Sulphate crystals ($\text{MgSO}_4 \cdot x\text{H}_2\text{O}$) yielded, on heating, 29 gram of the anhydrous salt. Determine the value of x .

PRACTICAL EXERCISES.

To measure the Contraction in Volume which occurs when Alcohol dissolves in Water. Use a long, thin graduated tube which holds either 50 c.c. or 100 c.c. when full. Place in it, first, half its volume of distilled Water, then, holding it in a slanting position, pour Alcohol slowly and carefully into it till it is full; if this is properly done, the two liquids will only mix to a small extent. Then place the thumb over the open end of the tube and cause the liquids to mix by shaking vigorously. When this is thoroughly accomplished read the final volume, and calculate the percentage contraction in volume.

To determine the Solubility of Potassic Chlorate at the temperature of the room. Make a strong solution of Potassic Chlorate in hot distilled water in a boiling tube and allow it to cool, when crystals must be deposited or more solid must be added, and the liquid warmed again. When cooled down to room temperature, place about 5 c.c. of the clear liquid above the crystals in a weighed porcelain crucible. Weigh the crucible and its contents, and then place it in a steam oven, and leave it till all the water has evaporated. When cool weigh again. The difference between the last two weights gives the weight of the water, and by subtracting the weight of the empty crucible from the last weight, the weight of Potassic Chlorate which was dissolved in the water can be found, and hence the weight dissolved by 100 grams of water can be calculated.

By keeping the boiling tube containing the saturated solution of Potassic Chlorate in a beaker of water maintained at various temperatures, the solubility of this salt at any temperature up to 60° C. can be ascertained by means of a similar experiment to the one described above, and a solubility curve for the Chlorate constructed by plotting the results obtained on squared paper.

To separate Mixtures by Solution. See Practical Exercises at the end of Chapter I.

On Supersaturation. Take about 20 grams of Sodium Thio-sulphate ("Hypo") in a boiling tube, and warm gently till the solid has dissolved in its own water of crystallization. Place a plug of cotton wool in the mouth of the test tube, fix the tube in the clamp of a retort stand and allow the contents to cool without shaking the liquid in any way. If no dust gets into the tube, crystals will not form, even when the liquid is quite cool. Now add a small crystal of "Hypo," note the rapid formation of crystals and, with a thermometer, measure the rise of temperature in the liquid.

To find the percentage of Water of Crystallization in Crystals of Copper Sulphate. Weigh a porcelain crucible and its lid; weigh into it not more than 1 gram of powdered Copper Sulphate crystals. Place the crucible and its contents about

1 inch above the tip of a small bunsen flame for 15 minutes. Cool in a desiccator and weigh again. Repeat the heating, cooling and weighing till the weight remains constant. The loss of Weight represents the Water of crystallization in the weight of crystals taken. Calculate the percentage loss in weight. A good result should be near 36 per cent.

To form an Overgrowth. Make a strong hot solution of Chrome Alum, and allow it to crystallize by slowly cooling the liquid. Take one of the best shaped octohedra formed and suspend it by a thread in a cold saturated solution of Potash Alum. Leave for two or three days, when an overgrowth of colourless Potash Alum should form on the mauve-coloured octohedron of Chrome Alum.

A similar overgrowth of colourless Potassic Sulphate may be made on a crystal of yellow Potassic Chromate.

CHAPTER IX.

NATURAL WATERS.

WATER in Nature undergoes what is termed by Physicists a Cycle of Operations, in that, after passing through a series of changes, it returns to its original state again.

The water on the surface of the earth, in seas, lakes, etc., evaporates very rapidly in the hot regions of the world, and its vapour, being lighter than air, rises through the atmosphere. The cooler upper layers of the air cause it to condense, forming tiny globules of water, which collect in the form of clouds. These tiny drops, under conditions which need not be entered into in this place, coagulate together, forming larger drops of water, which fall to the earth as rain, or, in some cases, as hail or snow.

Its subsequent history depends on the nature of the ground upon which it falls ; if the land is impervious to water, such as clay, it runs over its surface, collecting eventually into rills and streams, which join together forming rivers, and these, in their turn, flow into the sea from which the bulk of the water originally came.

Should the land upon which the rain falls be pervious to water, such as sandy or chalky ground, the water sinks through more or less rapidly, till it meets with an impervious stratum, above which it collects, and is eventually forced to the surface again along some line of weakness in the form of a spring. This spring forms the source of a stream which takes the course indicated above.

During all these changes the solvent power of the water

is being continuously exerted. When in the air, it dissolves the gases of the atmosphere ; when on the earth, or under the earth's surface, it exerts its power on the rocks and soils with which it comes into contact.

Natural waters are conveniently divided for purposes of study into four groups : (1) Rain Water, (2) Spring Water, (3) River Water, (4) Sea Water.

Rain Water. This form of water, being water distilled in Nature's laboratory, contains no solid impurities, except it has fallen through the impure air of towns, but only gases dissolved from the atmosphere.

Two of these play a most important part in the economy of Nature. The dissolved Oxygen is essential for the breathing of all fishes that live in rivers, lakes or seas, and the dissolved Carbonic acid gas enables the water to dissolve certain rocks, such as limestones, which are insoluble in water which does not contain it.

When evaporated, freshly fallen rain water leaves no visible or ponderable residue, but it has been discovered that the dish in which the evaporation has taken place possesses, for a time, radio-active properties (p. 483), evidently due to some substance which the water has acquired during its journey through the air.

Spring Waters. Water which percolates through the strata of the earth exerts its solvent power upon the rocks with which it comes into contact, and its dissolved impurities will therefore depend on the nature of these rocks.

Springs which rise in a country whose rocks are mainly of volcanic origin, such as granites or basalts, will contain practically no impurities, but the great majority of springs contain much dissolved mineral matter which is often of great medicinal value.

Such springs are found in England at Bath, Cheltenham, Harrogate, Tunbridge Wells, Woodhall Spa and other places, and contain, amongst other things, Salt, Borax, Epsom Salts, Glauber's Salts and Salts of Iron. Mineral waters which contain Iron are known as Chalybeate waters.

Very often water which has come from some depth contains gases dissolved in it to such an extent that it effervesces

naturally when it reaches the surface and the pressure on it is removed. The most common gas found is Carbonic acid gas, which occurs in the springs at Seltzer, Apollinaris, Rosbach and other places.

Sulphuretted Hydrogen gas is also occasionally found in spring waters ; such a spring occurs at Harrogate, and is of great value medicinally.



FIG. 32.—Stalactites and Stalagmites.

When water percolates through the land of a limestone country, it is able, by the aid of its dissolved Carbonic acid gas, to dissolve the chalk. If opportunity occurs for water thus charged to evaporate, the chalk is deposited. This is the origin of the so-called petrifying springs or wells, which will coat with chalk any article which is suspended, so that the water from the spring drips over it.

Sometimes such chalk-charged water drips from the roof of a cave. As the drop of water hangs from the roof for a time, evaporation proceeds, and a tiny deposit of chalk is left when the rest of the drop falls; this deposit grows with successive drops, eventually forming a large pillar of rock suspended from the roof of the cave, which is called a *Stalactite*. The water which drops to the floor or flows down the walls of the cavern forms similar deposits, to which the name *Stalagmite* is given. Very often deposits thus formed are of a crystalline nature and make a beautiful spectacle when illuminated by a bright light (Fig. 32)



FIG. 33.—Diagrammatic section of a Geyser.

It is a known fact that, on proceeding from the surface of the earth towards its centre, the temperature gradually rises, so that water which has percolated to any great depth reaches its boiling point, and may get far above it under the great pressure obtaining in these regions. Water, such as this, is able to dissolve large quantities of Silica or Sand (SiO_2), but when the spring, arising from such a source, reaches the surface, it is cooled and can no longer hold the Silica in solution, so deposits it round its orifice. These hot silicious springs, when they rise from a pipe, are called Geysers, and are found in Iceland and the Yellowstone Park, U.S.A. Around the orifice of a geyser is found a basin-shaped deposit of the Silica thrown down as the water cooled (Fig. 33).

At Whakarewewa in New Zealand a similar series of springs issue from fissures in the rock and, flowing downhill, have formed most gorgeously coloured terraces, consisting of crystalline deposits of white, pink and blue Silica.

River Waters. The nature and amount of dissolved impurities found in river water varies enormously, and is, of course, entirely dependent on the character of the rocks and soils over which it and its tributaries flow.

Thus the rivers of North Wales, Devon and Cornwall, and the Highlands of Scotland, flowing, as they do, through countries consisting mainly of insoluble granitic, basaltic and slaty rocks, contain a very small quantity of dissolved solids. The river Dee, for instance, at Aberdeen, contains less than $\frac{1}{6}$ part of dissolved matter in 10,000 of water.

On the other hand, a river like the Thames, which has most of its course in limestone countries, contains as much as 4 parts per 10,000 of dissolved matter, most of it Chalk, dissolved by the Carbonic acid gas in the water.

Rivers which flow through a clay country, *e.g.* the Trent, are found to contain Calcium Sulphate and Sodium Chloride in solution, which have been obtained from the beds of Gypsum and Salt which are interstratified with the clays.

Drinking Water. Since the supply of drinking water is almost entirely drawn from rivers, it is interesting at this point to consider how the impurities affect its potability, and how it can be ascertained whether a water is fit to drink or not.

Mineral impurities can all of them be detected by ordinary chemical analysis, and it is only in exceptional cases that they render a water unfit to drink, but germs of many diseases, such as cholera, typhus, etc., may be contained in the water in some quantity and yet be very difficult to detect.

River water which has been contaminated with sewage is always likely to contain these germs, and direct analysis would not shew their presence, but indirectly their presence may be inferred, if, on analysis, Nitrogen, though in infinitesimal quantity, is discovered to be present. The presence of this Nitrogen in the form of Nitrates, Nitrites or compounds

of Ammonium, is a sure sign that the water has been in contact with sewage matter, and any water which contains it should therefore always be treated with suspicion and never used for drinking purposes.

Sea Water. Since the rivers eventually discharge themselves with their dissolved impurities into the sea, from which pure water only is removed by evaporation, it naturally follows that sea water is most impure and tends to get more so as time goes on.

Water from the open sea contains about 34 parts of dissolved matter per 1000 of water made up roughly as follows :

Sodium Chloride, -	26.44	Magnesium Chloride, -	3.15
Magnesium Sulphate, -	2.07	Calcium Sulphate, -	1.33
Potassium Chloride, -	.75	Magnesium Bromide, -	.07
Calcium Carbonate, -	.05		

with traces of the Carbonates of Magnesium and Iron and the Chlorides of Lithium and Ammonium and of Silica.

This amount of solids is, of course, greater in land-locked seas ; the Mediterranean, for example, contains over 40 parts of dissolved matter per 1000 of water, whilst the Dead Sea, into which the Jordan and other rivers flow, but which has now no exit; contains the enormous quantity of 228 parts of solid per 1000 of water.

A study of the solids found in sea water is interesting. Salt forms by far the major portion, owing to its ready solubility ; any rock which may contain Salt loses it at once in contact with water, and, once in the sea, it does not get away again very readily. Chalk, on the other hand, which is present in great extent in the waters of most rivers, is almost absent in sea water. This is owing to the fact that it is taken out by all the animals in the sea which have shells. These animals, many of them, make extraordinarily good use of the small quantity present, for, in mid Pacific, where the water contains only .05 part of Chalk per 1000 of water, the coral polype builds up great coral islands and reefs from this very scanty supply of material.

HARDNESS OF WATER.

The presence of certain mineral salts in water gives rise to the property known as *Hardness*; the principal salts which cause it are the Carbonates and Sulphates of Calcium and Magnesium.

A hard water is so called because it will not, at first, form a lather with soap.

Soap consists of compounds of certain fatty acids (Oleic, Palmitic and Stearic) with the metal Sodium, and is soluble in water. When soap is brought into contact with salts of Calcium and Magnesium, the compounds of these metals and the fatty acids are formed, and these, being insoluble in water, are precipitated as "curds," and prevent the formation of lather, thus:

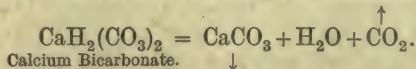
Sodium Stearate and Calcium Carbonate produce Sodium Carbonate and Calcium Stearate, this last-named salt being insoluble.

The hardness of water is usually expressed in degrees, each degree indicating the presence of 1 grain of Calcium Carbonate (or its equivalent in salts of Calcium or Magnesium) per gallon of water. Waters which contain little or no Calcium or Magnesium salts are said to be *soft*, and the process of removing these salts, either by precipitation or other means, is termed "softening" the water.

Hardness in water is of two kinds, *Temporary* and *Permanent*.

Temporary Hardness in water is caused by the presence of the Carbonates of Calcium and Magnesium. These salts are dissolved by the Carbonic acid gas in the water, and are supposed to exist in the form of Bicarbonates.

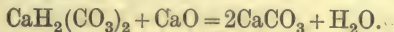
Temporary hardness can be got rid of by boiling the water; the Bicarbonates split up, Carbonic acid gas is evolved and the insoluble Carbonates are precipitated, thus:



This method of softening the water is, of course, inapplicable in the case of large volumes of water, and as the bye-laws of most towns forbid the supply of water of more than a certain

number of degrees of hardness, some other process of softening the water has to be adopted.

Clark's process is the one usually employed ; it consists in adding Lime to the water in the reservoirs ; this interacts with the Bicarbonates forming the Carbonates, which, being insoluble, are precipitated, thus :



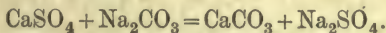
↓

Care must be taken that only the exact quantity of Lime necessary is added, as the addition of more would tend to harden the water, Calcium Hydrate acting as any other soluble Calcium compound.

The deposition of Chalk when temporarily hard water is boiled is the cause of the "furring" of kettles and the formation of "scale" in boilers. Both these are merely deposits of Chalk, and the formation of scale impairs very seriously the efficiency of a boiler, owing to the fact that it is a bad conductor of heat.

Permanent Hardness is caused by the presence of the Sulphates of Calcium and Magnesium in the water. The hardness is called Permanent, because such a water, being a dilute solution of a stable salt, is not softened by boiling.

In small quantities permanently hard water can be softened by adding Sodium Carbonate (Washing Soda) to the water ; this precipitates the Calcium as Carbonate, leaving Sodium Sulphate in solution, thus :



↓

A water thus softened is quite satisfactory for washing purposes, but is not pleasant to drink, owing to the bitter taste and medicinal qualities of the Sodium Sulphate.

Measurement of Hardness in Water. The hardness of two waters may be compared by the determination of the quantities of a soap solution which are needed to form a "permanent" lather with the same quantity of each of the waters. The criterion of a permanent lather is that it shall last for one minute.

Roughly speaking, if equal quantities of two different hard waters require 20 c.c. and 10 c.c. respectively of the same

soap solution to produce a permanent lather, the first water will be twice as hard as the second, and if the number of degrees of hardness present in either of the waters is known, the hardness of the other can be readily calculated.

PRACTICAL EXERCISES.

To find the Weight of Dissolved Solids in a Litre of Sea Water.

Weigh a porcelain dish, place in it, by means of a pipette, 25 c.c. of sea water and evaporate nearly to dryness. Add 25 c.c. more of the sea water and evaporate completely to dryness. Great care must be taken in the last stages of evaporation to avoid "spitting." Weigh the dish and its contents, and the increase in weight gives the weight of dissolved solids in 50 c.c. of sea water, whence the amount per litre can be readily calculated.

Tap water may also be used for this experiment.

Experiments on Hard and Soft Waters.

To make a soap solution. Cut up about 20 grams of Castile soap into small shavings and dissolve it in about 100 c.c. of boiling distilled water; make up the solution to 250 c.c. with distilled water.

To make some temporarily hard water. If the tap water is temporarily hard, it may be used for subsequent experiments. If not, dilute 25 c.c. of Lime water up to 100 c.c. and pass Carbon Dioxide gas through the liquid till the milkiness produced by the precipitation of Chalk is dissolved away. This makes a temporarily hard water.

To make a permanently hard water. If the tap water is permanently hard, it may be used. If not, dissolve about one-tenth of a gram of Plaster of Paris (Calcium Sulphate) in 250 c.c. of distilled water; this forms a permanently hard water.

To compare the hardness of different samples of water. Use a glass stoppered bottle, which, before each experiment, must be rinsed out with distilled water. Place 25 c.c. of distilled water in the bottle and put some soap solution, made as described above, in a burette. Add the soap solution carefully to the distilled water, shaking the bottle vigorously after

each addition, till a lather is produced which lasts one minute. This represents the quantity of soap solution necessary to form such a lather with pure water and must be subtracted from the amount added to a similar quantity of any hard water in order to obtain the quantity of soap solution needed to precipitate the Calcium or Magnesium salts in the water.

Now take 25 c.c. of temporarily hard water and find the quantity of soap solution necessary to form a "permanent" lather with it, and then perform a similar experiment with permanently hard water. By subtracting the quantity used for distilled water from the quantities used in each of the two cases, the hardness of the two kinds of water is directly proportional to the quantities added.

For example, if 25 c.c. of distilled water required 1.5 c.c. of soap solution, and 25 c.c. of temporarily hard and permanently hard waters required 9.4 and 7.6 c.c. of soap solution respectively, the hardness of the two waters is as 7.9 : 6.1.

To soften temporarily hard waters. (1) Boil some of the temporarily hard water for a full minute, allow to cool and prove that it is softened by finding how much soap solution is necessary to form a lather with 25 c.c. of it.

(2) Add about 5 c.c. of Lime water to 50 c.c. of the temporarily hard water. Then take 25 c.c. of it and find the quantity of soap solution needed to form a lather.

To soften permanently hard water. Add a little Sodium Carbonate solution to some of the permanently hard water, and determine if it is softer than before by adding soap solution to 25 c.c. of the water.

To make a standard hard water. Weigh out accurately .5 gram of powdered Calcium Carbonate. Dissolve it in a small quantity of Hydrochloric acid and evaporate to dryness in a porcelain dish. Dissolve the Calcium Chloride thus obtained in distilled water, pour the solution and the washings from the dish into a litre flask, and fill up to the mark with distilled water.

This solution represents a hardness of $\frac{1}{2}$ gram of Chalk per litre, and the hardness of any kind of water may be compared with it by similar experiments to those described above.

CHAPTER X.

OZONE AND HYDROGEN PEROXIDE.

OZONE.

Formula, O_3 . Molecular Weight, 48.

History. When a series of electric sparks are made for some time in an atmosphere of Oxygen, it acquires a peculiar smell ; this fact was observed by Van Marum (1785), but he did not ascertain the cause of it. Schonbein (1840) was the first to recognize that a new distinct substance was formed, and on account of its smell he gave it the name Ozone (Greek ὄζω, a smell). He also discovered that the same gas was formed, with the Oxygen, when water was electrolysed.

It is said that Ozone is present in air, especially in sea and country air ; this matter will be discussed later.

Formation. (1) If pure dry Oxygen is exposed to the influence of a silent electric discharge, it acquires the smell and the properties of Ozone, and is said to be ozonized.

A convenient form of the apparatus is shewn in the diagram (Fig. 34). Oxygen is slowly passed from *A* through the annular space between the two tubes *B* and *C*, which are of slightly different diameters and sealed together at the top.

N.B.—Rubber must not be used in any part of the apparatus, as it is attacked by Ozone.

The whole apparatus is immersed in a bath of dilute Sulphuric acid, and the same liquid is placed in the inner tube *C*. Platinum wires are immersed, one in the acid in *C* and

the other in the acid in the surrounding beaker, and these wires are joined to the two terminals of an induction coil.

On setting the coil to work, the Oxygen, as it passes through the annular space between the two tubes, is subjected to what is called a silent discharge of electricity of high voltage, and part of the Oxygen is converted into Ozone, which can be recognized by its smell and other tests as it emerges from the tube at *D*.

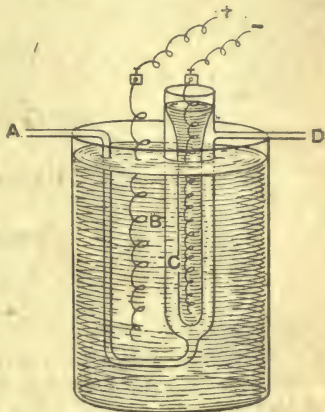


FIG. 34.—Preparation of Ozonized Oxygen.

(2) Ozone is formed in small quantities when a cleaned stick of yellow Phosphorus is allowed to remain in a jar full of air for a little time, the Oxygen in the air being partially converted into Ozone.

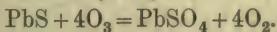
(3) The presence of Ozone can be detected in the Oxygen evolved at the positive pole during the electrolysis of acidulated water (see p. 112).

Properties. Ozone is a colourless gas, with a strong unpleasant smell somewhat similar to that of Chlorine. If strongly ozonized air is breathed, it causes headache, but in small quantities Ozone has a most refreshing effect.

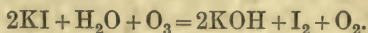
It is slightly soluble in water, but dissolves readily in essential oils, such as Turpentine or oil of Cinnamon.

It is a very powerful oxidizing agent; Ozonized Oxygen, when passed through a rubber tube, causes its rapid decay owing to oxidation. It bleaches Indigo and other vegetable colouring matter and attacks most metals with the formation of their Oxides.

Black Lead Sulphide is quickly changed by Ozone into white Lead Sulphate (cf. Hydrogen Peroxide).



When allowed to act upon a solution of Potassium Iodide it liberates the Iodine, forming Caustic Potash.



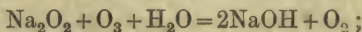
This action on Potassium Iodide forms a ready means of detecting Ozone, as the liberated Iodine can be recognized, in very small quantity, by its action on starch, which is turned blue by it. Iodized starch paper is merely filter paper which has been dipped in a solution of starch containing a little Potassium Iodide; such a paper will turn blue in Ozonized Oxygen or air.

A word of caution is needed with regard to this test. *Any strong oxidizing agent*—Hydrogen Peroxide, for instance—will liberate the Iodine from Potassium Iodide, and so will turn iodized starch paper blue, so that it is by no means certain that all specimens of air contain Ozone which answer this test: they may contain Hydrogen Peroxide; indeed, it is quite possible that this latter is the oxidizing agent in the case of sea air.

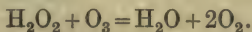
Ozone is decomposed in the presence of finely divided Platinum, Lead Peroxide, Silver or Copper Oxides, being converted into ordinary Oxygen; these substances are found to be unchanged at the end of the reaction, and hence it is a Catalytic one.

Thus Ozonized Oxygen, when passed through a tube containing black Copper Oxide, will no longer change the colour of iodized starch paper when it issues from the tube, but the Copper Oxide is found to be quite unchanged during the process.

The action of Ozone on Peroxides is interesting, as both the Peroxide and the Ozone have a loosely combined atom of Oxygen; these atoms tend to split off and combine with one another, forming a molecule of Oxygen; hence two strong oxidizing agents will mutually reduce one another. The equation in the case of Sodium Peroxide is



with Hydrogen Peroxide,



The decomposition of Ozone into Oxygen takes place slowly at ordinary temperatures, but the velocity of the change rapidly increases with the temperature, and, if Ozone is heated for a very short time to 300°C. , it is entirely decomposed.

Composition of Ozone. From the facts that Ozone can be made by passing a silent discharge through pure Oxygen, and that, when Ozone is heated, the resultant gas contains nothing but Oxygen, it is reasonably inferred that Ozone contains nothing but Oxygen.

When a solution of Potassium Iodide is placed in a closed vessel containing Ozonized Oxygen, though decomposition takes place there is no contraction of volume. One molecule of Oxygen is liberated for every molecule of Ozone which is decomposed, and, since some Oxygen must have been necessary to liberate the Iodine from the Potassium Iodide, it is clear that the molecule of Ozone must contain more Oxygen atoms than the molecule of Oxygen.

Now the number of Oxygen atoms per molecule is 2, and so the number of Oxygen atoms in a molecule of Ozone must be more than 2.

The actual number is well established by an experiment of Soret (1866). He subjected measured volumes of the same specimen of Ozonized Oxygen (1) to the action of Turpentine, which dissolved the Ozone only, and consequently a diminution in volume took place and was measured; (2) to the action of heat by passing it through a hot tube containing broken porcelain, which caused the Ozone to change into Oxygen, and a measured increase in the volume took place.

Diagrammatically Soret's results are seen in the diagram (Fig. 35). In tube I. the result of the action of Turpentine is seen by the volume diminishing from the level *A* to level *B*, hence *AB* represents the volume of Ozone present; in tube II. the result is seen by the increase in volume from level *C*

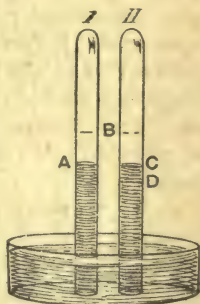


FIG. 35.—Diagrammatic figure for proving the Formula for Ozone.

to level *D*. It is found that, with exactly the same volume of the original gas, the increase *CD* is half the decrease *AB*.

Comparing these results, it is clear that a volume of Oxygen represented by *BD* has been formed from a volume of Ozone represented by *AB*, which is two-thirds of *BD*.

That is, 3 volumes of Oxygen have been formed from 2 volumes of Ozone.

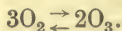
If Avogadro's Hypothesis is accepted,

3 molecules of Oxygen = 2 molecules of Ozone.

But 3 molecules of Oxygen contain 6 atoms of Oxygen.

Hence each molecule of Ozone must contain 3 atoms, and its formula is O_3 .

The change from Oxygen to Ozone is a reversible one, and is represented by the equation



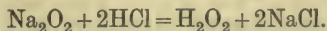
HYDROGEN PEROXIDE.

Formula, H_2O_2 . Molecular Weight, 34.016.

Occurrence. Hydrogen Peroxide has been detected in very small quantities in air, in freshly fallen rain water and in snow.

Preparation. When a jet of burning Hydrogen is made to impinge on the surface of ice-cold water, Hydrogen Peroxide can be detected in the water.

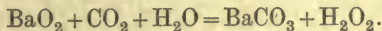
It is usually prepared from Peroxides by acting upon them with dilute acids. For example, Sodium Peroxide and dilute Hydrochloric acid yield a mixture of Hydrogen Peroxide and Sodium Chloride :



If Potassium Peroxide and Tartaric acid are used, the Potassium Tartrate formed can be made to separate out by keeping the liquid ice cold, and a fairly pure solution of Hydrogen Peroxide is obtained.

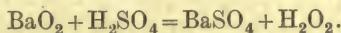
On the large scale Peroxide of Barium is used ; by passing carbonic acid gas through ice-cold water, to which small

quantities of the Peroxide are added from time to time, Barium Carbonate is precipitated, and a dilute solution of Hydrogen Peroxide remains:



↓

If Sulphuric acid is used, very dilute acid must be gradually added to a well cooled mixture of Barium Peroxide and water till the resulting liquid is just acid to litmus, then sufficient Barium Monoxide (BaO) is added to neutralize the excess of Sulphuric acid, and, on filtering from the precipitated Barium Sulphate, a fairly pure dilute solution of Hydrogen Peroxide is obtained:



↓

Dilute solutions obtained in these ways cannot be concentrated by boiling owing to the unstable nature of the

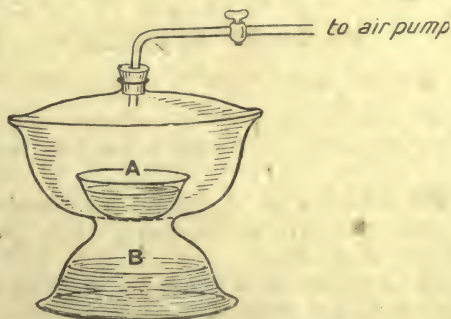


FIG. 36.—Evaporation in Vacuo.

Hydrogen Peroxide; they can be concentrated to a point when the liquid contains 45 per cent. of Hydrogen Peroxide, by slow evaporation over a water bath at a temperature of $70^{\circ}\text{C}.$, but the pure Peroxide can only be obtained by evaporation in vacuo.

A dilute solution of Hydrogen Peroxide is placed in a porcelain dish (*A*) in a desiccator containing Sulphuric acid (*B*) (Fig. 36) as the dehydrating agent; the lid is firmly greased

on and connected by a tube to a good air pump. Under the reduced pressure the water evaporates, but, being at once absorbed by the acid, further evaporation continually takes place, and eventually practically pure Hydrogen Peroxide is left.

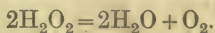
N.B.—Owing to the Latent Heat of Evaporation of the water, the liquid in the dish remains at a very low temperature, so that no decomposition takes place.

Properties. Hydrogen Peroxide is a colourless viscid liquid of Sp. Gr. 1.46. It has no smell and dissolves in water in all proportions. It is generally used in dilute solutions, the strengths of which are represented by the number of times its volume of Oxygen which the solution evolves on decomposition. Thus 100 c.c. of a 10 volume solution of Hydrogen Peroxide will evolve 1 litre of Oxygen when completely decomposed.

Decomposition takes place rapidly when the liquid is boiled or when a Catalytic agent such as Platinum black (or any powdered metal) or Manganese Dioxide is dropped into the solution; if pure Hydrogen Peroxide is used, decomposition occurs with explosive violence.

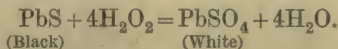
A few drops of pure Hydrogen Peroxide dropped on to cotton wool decompose with sufficient evolution of heat and Oxygen to cause the wool to inflame.

In all cases of decomposition Water and Oxygen are formed :



On account of this readiness for evolving Oxygen, Hydrogen Peroxide is a very strong oxidizing agent; it will liberate Iodine from Potassium Iodide in a precisely similar manner to Ozone.

If a strip of filter paper is moistened with a solution of Lead Acetate, and then held in a jet of Sulphuretted Hydrogen gas, it is blackened owing to the formation of Lead Sulphide; if now this black deposit of Sulphide is treated with a solution of Hydrogen Peroxide, it becomes white, owing to the formation of Lead Sulphate by oxidation :



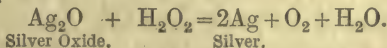
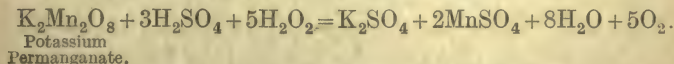
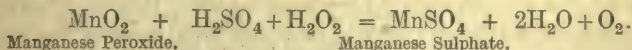
This reaction is made use of in the restoration of old pictures blackened by age. The basis of most paints is Lead Carbonate (White Lead); this compound, by the action of Sulphur contained in coal gas and in other products of combustion and decomposition, is changed into Lead Sulphide, and the original colours are restored by the above-mentioned process.

Owing to its oxidizing properties, Hydrogen Peroxide takes the colour away from many dyes, such as Indigo and Litmus; it is therefore used, to some extent, as a bleacher, especially for fabrics, such as silk, feathers, straw, etc., which are injured by more violent bleaching agents. The human hair is also bleached by it to the, at one time, fashionable straw colour.

Because of the ease with which it parts with its Oxygen, Hydrogen Peroxide is much used as a disinfectant, and many of the modern preparations for cleansing the teeth contain it.

A very delicate test for Hydrogen Peroxide is given by its formation of a deep blue colour with a solution of Potassium Bichromate. This test applies to very dilute solutions in the following manner. A small quantity of Ether is first added to the solution and, on shaking, most of the Peroxide is dissolved out by the Ether, then the addition of a few c.c. of Potassium Bichromate and a further shaking causes the layer of Ether to assume a deep indigo blue colour.

As was seen with Ozone, the action of Hydrogen Peroxide on other oxidizing agents is to cause the mutual reduction of both. Equations are appended for one or two cases, and they explain themselves:



Formula of Hydrogen Peroxide. Thénard (1818), by decomposing pure Hydrogen Peroxide and weighing the resultant products, found that 17 parts by weight of the Peroxide yielded 8 parts of Oxygen and 9 parts of Water.

This means that Hydrogen Peroxide contains Hydrogen and Oxygen in the proportion of 1 atom of Hydrogen to 1 atom of Oxygen. Its simplest formula would therefore be HO or some simple multiple of it, of the form H_nO_n .

Owing to its unstable nature, its density in a state of vapour cannot be determined, but its molecular weight has been ascertained by the Freezing Point Method (p. 151), and is found to be approximately 34. This leads to the formula H_2O_2 , which is the one generally accepted.

PRACTICAL EXERCISES.

To prepare Ozonized Oxygen and examine its Properties. Oxygen containing a small percentage of Ozone can be readily obtained by the electrolysis of acidulated water in an apparatus

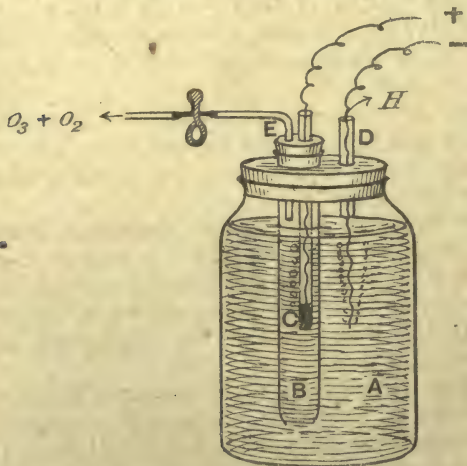


FIG. 37.—Preparation of Ozonized Oxygen.

like that in the diagram (Fig. 37). *A* is a wide-mouthed bottle containing water acidulated with Sulphuric acid. Through the large cork pass a boiling tube *B*, with its closed end

broken off, and a short piece of glass tubing open at both ends, through which passes the Platinum wire connected with the negative electrode of the battery. Through the cork of the boiling tube are passed two tubes; one, *C*, has its lower end closed and a short piece of Platinum wire fused through it; the lower part of this tube has some Mercury in it, and this is connected with the positive electrode of the battery by a Copper wire; the other, *E*, serves for the exit of the Ozonized Oxygen, and is fitted with a piece of rubber tubing and a clip.

After the current has passed for some time, Ozonized Oxygen collects in the boiling tube, and its properties may be examined by opening the clip.

Allow it to act upon some filter paper dipped in a mixture of Potassium Iodide solution and Starch, and observe the blue "Iodide of Starch" produced. Also on a filter paper dipped in Indigo solution, and notice its bleaching action. Also dip a filter paper in a solution of Lead Acetate, hold it in a jet of Sulphuretted Hydrogen to change it into black Lead Sulphide, then hold it in the Ozone and notice that it is changed into white Lead Sulphate.

Next, attach a tube containing powdered Copper Oxide to the Ozone jet, and try the same experiments again. Notice that no changes occur in any case owing to the Ozone being broken down into Oxygen.

To prepare Hydrogen Peroxide and examine its Properties. Take about 10 grams of Barium Peroxide in a boiling tube, add 30 c.c. of dilute Hydrochloric acid and mix well, keeping the boiling tube cool by immersion in cold water. Filter away any sediment that remains, and the filtrate will contain Hydrogen Peroxide.

Try the effect of this liquid upon the same substances as used for Ozone, viz. Iodized Starch paper, Indigo and Lead Sulphide. Notice a precisely similar action to that of Ozone.

Also add to the liquid some Ether and then a few c.c. of a solution of Potassium Bichromate; shake up together and notice the deep blue coloration acquired by the Ether.

CHAPTER XI.

LAWS OF CHEMICAL COMBINATION.

UNTIL the close of the eighteenth century, the balance was very little used, for accurate work at any rate, in the study of chemical reactions, and the quantitative laws which govern these reactions were not even suspected, but, starting about 1780, very accurate investigations, conducted by Lavoisier, Dalton, Berzelius and Gay-Lussac, amongst others, brought about the establishment of four laws of Chemical Combination.

I. Law of Definite Proportions. This may be stated thus :

"A given chemical compound, however it is made, always contains the same elements united together in the same proportions." This law was definitely established by Proust (1806) from the results of a great number of analyses by himself and other chemists of that time. It puts forward the fact that Salt, for instance, whether it comes from the salt mines of Galicia or Cheshire, from sea water, or by causing Sodium to burn in Chlorine gas, always contains the elements Sodium and Chlorine *only*, and in the exact proportion of 1 of Sodium to 1.54 of Chlorine, by weight.

A simple way of ascertaining the truth of this law is to change a fixed weight—1 gram—of Copper into Copper Oxide by several different processes, taking great care that nothing is lost during the experiments, and weighing accurately the Copper Oxide produced in each case.

Three methods of producing this change are :

(1) By heating precipitated Copper in a stream of air till no further increase of weight occurs.

(2) By dissolving the Copper in dilute Nitric acid, evaporating the solution to dryness, and heating the resulting Copper Nitrate till it yields Copper Oxide and its weight is constant.

(3) By dissolving the Copper in dilute Nitric acid, adding Caustic Potash to precipitate the whole of it as Copper Hydrate, boiling the Hydrate till it changes completely into black Copper Oxide, and filtering and drying this black residue.

In all these cases it is found, if the experiments are carefully performed, that 1 gram of Copper yields 1.254 grams of Copper Oxide.

A similar series of experiments may be made to prove this law by Analysis instead of Synthesis. Copper Oxide may be prepared in several different ways, and, if 1 gram of it is reduced to Copper by passing Hydrogen or Coal gas over it, heated to redness in a bulb tube, the same weight of Copper —.79 gram—will be found remaining in each case.

If, in the formation of a chemical compound by direct union (*e.g.* Copper Sulphide from Copper and Sulphur), a greater weight of either element is used than is necessary for the exact proportion, the excess weight of this element will be found unchanged and uncombined at the end of the experiment.

II. Law of Multiple Proportions. This states that :

“ When two elements unite together in different proportions to form different compounds, then, if a fixed weight of one of these elements is taken, the weights of the other element which combine with this fixed weight bear a simple multiple relation to one another.”

This law was first put forward by Dalton, as the result of his examination of the composition of the two compounds of Carbon and Hydrogen, Marsh gas and Ethylene. He discovered that, in Marsh gas 1 part of Hydrogen unites with 3 parts of Carbon, while the proportions in Ethylene are 1 of Hydrogen to 6 of Carbon.

A similar proportionality is seen in the four compounds which Nitrogen forms with Oxygen.

Nitrous Oxide contains 1 of Nitrogen and .571 of Oxygen.

Nitric Oxide „ 1 „ „ 1.143 „

Nitrogen Peroxide contains 1 of Nitrogen and 2.286 of Oxygen.

Nitrogen Pentoxide contains 1 of Nitrogen and 2.857 of Oxygen.

These weights of Oxygen, if examined, are found to be in the proportions 1 : 2 : 4 : 5.

A practical demonstration of the truth of this law may be made by taking known weights of the two Oxides of Copper, red Cuprous Oxide and black Cupric Oxide, reducing each to the metal by passing Hydrogen or Coal gas over them, and weighing the Copper contained in each specimen. It will be found that 1 gram of Copper combines with .126 gram and .252 gram of Oxygen in the two cases, and these numbers are simple multiples of one another.

III. Law of Reciprocal Proportions.

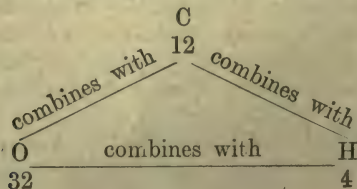
This may be stated thus:

“The proportions in which two elements, A and B, combine with a fixed weight of a third element, C, represent the proportions in which they will themselves combine, if union between them is possible, or they bear some simple relation to these proportions.”

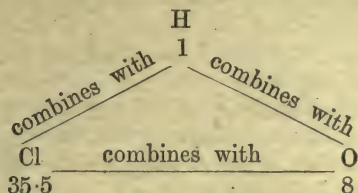
This law was put forward by Richter, largely as the result of many careful analyses by Berzelius.

If the two chief compounds which Carbon forms with Oxygen and Hydrogen are analysed, it is found that, in Carbon Dioxide, 12 of Carbon combine with 32 of Oxygen, whilst in Marsh gas, 12 of Carbon unite with 4 of Hydrogen. This law states that, if Oxygen and Hydrogen unite, they will do so in the proportion of 32 of Oxygen to 4 of Hydrogen (or some simple multiple of these proportions), and it is a fact that these numbers represent the proportion of Hydrogen and Oxygen found in water.

This may be expressed in the form of a diagram, thus :



Another example shewing the combinations of Hydrogen, Chlorine and Oxygen is shewn, thus :



These three Laws refer to the proportions in which elements unite *by weight*; a fourth Law, put forward by Gay-Lussac, and usually called after him, refers to the proportions *by volume* in which gases combine.

IV. Law of Volumes. This law is stated thus :

"When gases combine, they do so, either in equal volumes or in volumes which bear some simple relation to one another and to the volume of the resulting product, if gaseous."

This is usually called Gay-Lussac's Law.

Examples which bear out this Law are seen (1) when 1 volume of Hydrogen unites with 1 volume of Chlorine to form 2 volumes of Hydrochloric acid gas, (2) when 2 volumes of Hydrogen combine with 1 volume of Oxygen to form 2 volumes of Steam, (3) when 2 volumes of Carbon Monoxide unite with 1 volume of Oxygen to form 2 volumes of Carbon Dioxide. It must be noted that the volumes of the reacting gases and of their products must all be measured at the same temperature and pressure.

ATOMIC THEORY.

Ancient philosophers of India, Greece and Italy had many theories as to the constitution of matter. Their ideas were, of course, purely guess work, but many of their guesses came remarkably near the truth, as we understand it at the present time.

They taught, for instance, that matter is composed of atoms separated by void spaces, and that these atoms were in

constant motion. The atoms were also supposed to be quite indestructible, and the different properties of different substances were supposed to be due to the different nature of the atoms composing them or to different methods of their arrangement.

The extraordinary accuracy of these speculations—for such they must be considered—is only to be attributed to chance, for, apparently, they possessed no facts upon which to build their theories, whereas the modern Atomic Theory is based upon actual chemical facts.

Modern philosophers, such as Bacon, Descartes, Boyle and Isaac Newton, possessed similar ideas on the structure of matter, but it was not till 1801 that John Dalton put forward his Atomic Theory, using as his basis the Laws of Chemical Combination which have just been discussed.

Dalton suggested that chemical combination took place between definite small quantities of each element, which he called *Atoms*. He defined an Atom as “the smallest quantity of an element which can exist in combination”; he considered that every elementary substance is made up of these Atoms, which, for the same element, are all alike in size, weight and other properties, but differ in different elements.

Certain of these Atoms possess the power of uniting with other Atoms, either of the same or another element, and the groups of Atoms thus formed are called *Molecules*.

A *Molecule* is defined as “the smallest quantity of any substance, whether element or compound, which can exist by itself.”

In an element the molecules are made up of similar atoms, but, in a compound, though each molecule is similar to every other molecule in the compound, the molecules themselves are composed of dissimilar atoms.

The chemical attraction which some atoms have for others is called “Chemical Affinity,” and the reason why some atoms have this affinity for one another and none at all for other different atoms is not understood at present.

Molecules are by no means large; their size, in the case of Water, has been well expressed by Lord Kelvin when he says that, if a drop of water is magnified till it is as large as the

earth, the contained molecules will be about as large as a cricket ball.

When two elements unite, one or more atoms of the one are supposed to combine with one or more atoms of the other, to form a molecule of the compound, and, since there must be a definite number of atoms of each element (for, by hypothesis, nothing smaller than an atom can exist), it is clear that combination must take place in definite proportions of each element, which statement is in accordance with the first Law of Chemical Combination. Again, if more than one compound is formed by two elements uniting together, since only multiples of single atoms can unite, the resulting proportions of the two elements in the two compounds must be simple multiples of one another, which is in accordance with the second Law of Chemical Combination, and the third Law of Reciprocal Proportions follows in a precisely similar manner.

THE KINETIC THEORY OF MOLECULES.

It has already been seen that liquids and gases certainly, and solids to some extent, diffuse the one into the other. It is evident, from this, that matter cannot be a continuous medium, for two continuous media cannot occupy the same space. Moreover, gases can be readily compressed, and liquids and solids are also compressible to a certain extent; this could not happen if matter were continuous.

Matter, then, is said to be discrete and made up of molecules. These molecules must be in a state of continuous motion or diffusion could not take place. In a gas, this motion is supposed to occur in all directions, and the constant battering of gaseous molecules on the walls of the containing vessel constitutes the pressure of the gas.

In a gas, the molecules are very thinly packed together—it has been estimated that of every cubic foot of gas, one cubic inch, only, is occupied by matter—but, by the incessant and rapid motion of the molecules, it appears to fill the whole space.

In a liquid, the molecules are much more tightly packed together, the collisions between the moving molecules are much

more frequent, and diffusion takes place much more slowly than in gases.

The very small amount of compressibility of a solid and the fact that solids keep their shape almost indefinitely, shew that the mobility of solid molecules is but small. Nevertheless, though molecules are incapable of motion from one part of a solid to another, they are in a state of rapid vibration, to and fro, each in its own fixed position.

It has been calculated that, in most solids, matter fills barely one quarter of the space apparently occupied by the solid, and the appearance of solidity is due to this rapid vibration of the molecules, in much the same manner as a cycle wheel appears as a solid disc if rotated rapidly enough.

AVOGADRO'S HYPOTHESIS.

If Dalton's Atomic Theory of Chemical Combination is considered in conjunction with Gay-Lussac's Law of Volumes, that is, if, firstly, one or more atoms of one element combine with one or more atoms of another element, and, secondly, elements in a gaseous state unite in simple proportions by volume, it must follow that the number of atoms in similar volumes of gaseous elements bear some simple relation to one another.

To illustrate this further: Oxygen and Hydrogen unite in the proportion of 1 : 2 by volume. Dalton assumes that combination takes place between *atoms* of Oxygen and *atoms* of Hydrogen; hence it would seem likely that the number of atoms of Oxygen and Hydrogen in a given volume are either equal or bear some simple relation to one another.

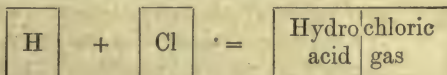
Gay-Lussac was the first to suggest that equal volumes of all gases contain an equal number of atoms. On that hypothesis, when 2 volumes of Hydrogen combine with 1 volume of Oxygen to form 2 volumes of Steam, then $2n$ atoms of Hydrogen must combine with n atoms of Oxygen to form $2n$ compound atoms of Steam, or, more simply, 2 atoms of Hydrogen and 1 atom of Oxygen form 2 atoms of Steam, from which it is clear that 1 atom of Oxygen must have split in half in order to make parts in 2 compound atoms of Steam, whereby the idea of the indivisibility of the atom is completely contradicted.

Avogadro (1811) was the first to point this out, and he found a way out of the difficulty by suggesting that the word molecule should be substituted for atom, and the Hypothesis which now bears his name runs thus: "*Equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules.*"

He considered that a certain fixed number of atoms in each element are combined together to form a molecule of that element, and that, in a compound, a similar union of the different atoms of the elements contained in the compound forms a molecule of the compound.

Accepting this Hypothesis of Avogadro, consider the case of the union of Hydrogen and Chlorine to form Hydrochloric acid gas. It is found, by experiment, that 1 volume of Hydrogen and 1 volume of Chlorine unite to form 2 volumes of Hydrochloric acid gas.

Expressing this result graphically:

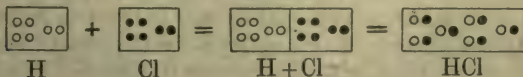


By Avogadro's Hypothesis it follows that n molecules of Hydrogen unite with n molecules of Chlorine to form $2n$ molecules of Hydrochloric acid gas.

Now each of these molecules of Hydrochloric acid cannot contain less than 1 atom of Hydrogen and 1 atom of Chlorine, and it will be seen later that each molecule actually does contain 1 atom of each element. Hence it follows that every molecule of Hydrogen has formed two molecules of Hydrochloric acid gas, each containing 1 atom of Hydrogen, and therefore the molecule of Hydrogen itself must contain 2 atoms of Hydrogen.

With similar reasoning, it is easily seen that each molecule of Chlorine contains 2 atoms of Chlorine.

Another graphical way of representing this action is:



In a similar way it has been established that the molecules of all the elementary gases—Hydrogen, Oxygen, Nitrogen, Chlorine and Fluorine—contain, at ordinary temperatures, 2 atoms.

This Hypothesis of Avogadro's has been tested in numerous ways, and never found wanting, and it has given such a reasonable explanation of many natural phenomena that it is now accepted as a fundamental truth, and is usually known as Avogadro's Law.

It is not, strictly speaking, a Law, because its truth cannot be actually tested, but, in that respect, it has the same standing as Newton's Laws of Motion, which are in a precisely similar position.

PROBLEM.

16. A metal has two Oxides *A* and *B*. 1 gram of *A* yielded, on reduction, .798 gram of the metal. 1 gram of *B*, treated in the same manner, gave .888 gram of the metal. Shew that these results are in agreement with the Law of Multiple Proportions.

PRACTICAL EXERCISES.

To prove the Law of Definite Proportions.

First method. Change metallic Copper into Copper Oxide by two different methods, and shew that the same proportion of Oxide is produced in each case.

Take a hard glass tube about 15 cm. long, weigh it and place in it some pure precipitated Copper, and weigh again. Then heat the tube and pass Oxygen (from a cylinder) slowly over the Copper. Weigh when cool, then pass more Oxygen through the heated tube and weigh again. Do this till the weight is constant. The increase in weight gives the weight of Oxygen absorbed. Calculate the weight of Oxygen which has combined with 1 gram of Copper.

To attain the same result in another way, take a weighed amount of Copper in a porcelain crucible, add strong Nitric acid slowly till the Copper is all dissolved. Evaporate gently, with the lid partly open, till Copper Nitrate is formed in the crucible, then heat strongly to change the Nitrate into Oxide

of Copper. Find the weight of Oxygen which has combined with the known weight of Copper, and calculate the weight of Oxygen which would combine with 1 gram of Copper.

The results should be exactly the same in the two cases.

Second method. Prepare Copper Oxide by three distinct methods, reduce it to Copper, and find the proportion of Copper to Oxygen in the three specimens of Oxide.

- (1) Obtain Copper Oxide by heating Copper Carbonate strongly in a porcelain crucible.
- (2) Get a second specimen of Oxide by treating Copper Nitrate in a similar manner.
- (3) A third specimen is obtained by adding Caustic Potash to a solution of Copper Sulphate. Boil the liquid till the precipitate is black, filter and wash the precipitate on the filter paper well. Dry on a cone over a sand bath, and transfer the dried precipitate to a porcelain crucible and heat strongly.

Then take a known weight of each of the three specimens of Copper Oxide in a short piece of hard glass tubing, and reduce it to Copper by heating it and passing Hydrogen or Coal gas through the tube. The loss of weight gives the weight of Oxygen in each case, and from the results the percentage of Oxygen in Copper Oxide can be calculated. It should be exactly the same in all three specimens.

N.B.—Copper Oxide should always be heated immediately before weighing, as it rapidly absorbs water from the air.

To prove the Law of Multiple Proportions. By the preceding experiments, the weight of Oxygen which is combined with 1 gram of Copper in black Copper Oxide has been determined. Now dry some red Copper Oxide in a steam oven, and reduce a known weight of it in a heated glass tube by passing Hydrogen or Coal gas over it. From the results obtained, calculate the weight of Oxygen combined with 1 gram of Copper in the red Copper Oxide. It should be found to be exactly half that obtained for the black Oxide.

CHAPTER XII.

EQUIVALENTS AND ATOMIC WEIGHTS.

EQUIVALENT WEIGHT.

THE Laws of Chemical Combination, put forward in the last chapter, being accepted, it follows—particularly from the Law of Reciprocal Proportions—that there are definite fixed proportions, by weight, in which the elements unite together, and hence, if a standard or unit is adopted, definite numbers can be assigned to each element, signifying the weight of it which combines with or reacts with other elements.

The standard usually adopted is 1 gram of Hydrogen, as Hydrogen is the lightest known substance.

The Combining or Equivalent Weight of an element is that weight of it which combines with, or replaces, 1 gram of Hydrogen.

For example, in Water, 1 gram of Hydrogen is combined with 8 grams of Oxygen, so that the equivalent of Oxygen is 8; whilst in common Salt, NaCl , 23 grams of Sodium is taking the place of 1 gram of Hydrogen, so that the equivalent of Sodium is 23.

DETERMINATION OF EQUIVALENTS.

Method I. By Combination with Hydrogen. If an element combines directly with Hydrogen, and the weights of the element and the resultant compound can be determined experimentally, the weight of the element which combines

with 1 gram of Hydrogen can be easily calculated. For instance, in Dumas' celebrated experiment on the gravimetric synthesis of water (p. 72) it was found that 8 grams of Oxygen combine with 1 gram of Hydrogen, and therefore 8 is the Equivalent Weight of Oxygen.

The equivalent of Chlorine is found by allowing Hydrogen and Chlorine gases to unite directly. They are found to unite in equal proportions, by volume, but Chlorine is 35.5 times as heavy as Hydrogen; therefore the weights of equal volumes are in the proportion of 35.5:1, and hence 35.5 grams of Chlorine combine with 1 gram of Hydrogen, and this number is taken as the equivalent of Chlorine.

Method II. By Displacement of Hydrogen. Certain elements, which are all of them metals, will replace the Hydrogen in water, dilute acids and other substances, which Hydrogen is evolved as a gas during the reaction.

If the Hydrogen thus evolved from a certain weight of the metal is carefully collected and measured, its weight can be calculated from the known fact that 1 c.c. of Hydrogen at standard temperature and pressure weighs .00009 gram. Hence the weight of the metal which displaces 1 gram of Hydrogen, *i.e.* its equivalent weight, can readily be calculated.

In this manner the Equivalents of Sodium and Potassium can be found by using Methylated Spirits; Calcium, by using Water; Magnesium, Zinc, Iron and Aluminium, by using dilute Hydrochloric acid, and Zinc and Aluminium will drive out an equivalent weight of Hydrogen from a boiling solution of Caustic Potash.

Example. .27 gram of Magnesium, placed in dilute Hydrochloric acid, evolved 259 c.c. of Hydrogen gas collected over water at 12° C. and 765 mm. pressure. Calculate the equivalent of Magnesium.

Since the gas is collected over water, the maximum vapour pressure of water at 12° C. must be allowed for; this is 10.5 mm., and hence the "partial pressure" of the Hydrogen gas itself is

$$765 - 10.5 = 754.5 \text{ mm.}$$

This volume corrected to 0° C. and 760 mm. is

$$259 \times \frac{754.5}{760} \times \frac{273}{285} = 246.3 \text{ c.c.}$$

Its weight, therefore, is $246.3 \times .00009 = .0221$ gram.

Whence .0221 gram Hydrogen = .27 gram Magnesium,

$$\text{and } 1 \text{ gram Hydrogen} = \frac{.27}{.0221} = 12.2 \text{ grams Magnesium.}$$

In other words, the Equivalent Weight of Magnesium is 12.2.

Comparatively few of the elements will either combine with or replace Hydrogen directly by the methods indicated above, consequently their equivalents must be determined by indirect methods.

Since 1 gram of Hydrogen combines with 8 grams of Oxygen and 35.5 grams of Chlorine respectively, it follows that the equivalent weight of any element can be found by ascertaining what weight of it combines with either 8 grams of Oxygen or 35.5 grams of Chlorine.

Method III. By Combination with Oxygen. The method employed may be either that of Synthesis or Analysis.

If the equivalent is to be determined by Synthesis, most elements will unite directly with Oxygen if heated in a stream of it, and the resultant Oxide can be collected and weighed. Should the Oxide be gaseous or volatile at the temperature of the experiment—*e.g.* the Oxides of Sulphur, Carbon or Phosphorus—it may be led into a suitable absorbent, such as Caustic Potash in the above-mentioned cases, and the increase in weight of this absorbent gives the weight of Oxide formed. A suitable apparatus is shewn in the diagram (Fig. 38).

In the case of most metallic elements the Oxides are non-volatile, and a weighed quantity of the metal may simply be heated in a crucible in air or in a bulb tube, through which a gentle stream of Oxygen is passed, and the increase of weight gives the weight of Oxygen which has combined with the metal.

A better method, in the case of some metals, consists in

dissolving a weighed amount of the metal in Nitric acid in a porcelain crucible or dish, evaporating carefully till the water and acid are driven off, leaving the Nitrate of the metal, and then heating this Nitrate to dull redness, when Nitric fumes and Oxygen are evolved, and the Oxide is left behind and can be weighed. This method can be applied to all the commoner metals—except Gold and Platinum, which do not dissolve in Nitric acid,—and the Alkali metals, whose Nitrates do not yield Oxides at a dull red heat.

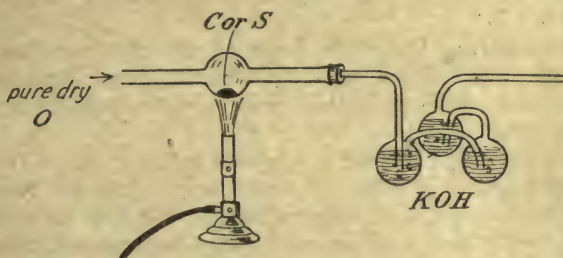


FIG. 38.—Determination of Equivalent by union with Oxygen.

Example. 2.4 grams of Lead, when dissolved in Nitric acid and the resulting solution evaporated to dryness and heated to dull redness, yielded 2.585 grams of Lead Oxide. Calculate the equivalent of Lead.

Here the weight of Oxygen which has combined with the Lead is $2.585 - 2.4 = .185$ gram.

Hence .185 gram of Oxygen combines with 2.4 grams of Lead, *i.e.* 8 grams of Oxygen combine with $\frac{2.4 \times 8}{.185} = 103.8$ grams of Lead.

Hence the equivalent of Lead = 103.8.

When the equivalent of an element with respect to Oxygen is to be determined by Analysis, the heated Oxide (which must be metallic) is reduced in a current of Hydrogen or Coal gas, and the loss of weight during the operation gives the amount of Oxygen which combines with the weight of metal left at the conclusion of the experiment.

Example. 1.64 grams of Copper Oxide left, on reduction by Hydrogen, 1.31 grams of Copper. Find the equivalent of Copper.

Here the loss of weight is .33 gram, which represents the weight of Oxygen which was combined with 1.31 grams of Copper.

Hence 8 grams of Oxygen combine with $\frac{8 \times 1.31}{.33} = 31.76$ grams of Copper.

Hence the equivalent of Copper is 31.76.

Method IV. By Combination with Chlorine. Several elements, such as Gold, Silver and Platinum, do not combine with Oxygen at all readily, nor are their Oxides very stable compounds. On the other hand, these elements combine readily with Chlorine to form stable Chlorides, and, since the equivalent weight of Chlorine is known to be 35.5 grams, the equivalent weights of these elements can be determined either from the increase in weight observed when Chlorine gas is passed over a weighed quantity of the heated metal, or from the decrease in weight when a known weight of the Chloride of the metal is reduced by passing Hydrogen over it.

The calculations proceed on exactly the same lines as when Oxygen is used.

Example. 1.54 grams of Silver, when heated in a current of Chlorine gas, yielded 2.05 grams of Silver Chloride.

Calculate the equivalent of Silver.

Here it is seen that .51 gram of Chlorine combines with 1.54 grams of Silver.

Hence 35.5 grams of Chlorine combine with $\frac{1.54 \times 35.5}{.51} = 107.2$ grams of Silver.

Hence the equivalent weight of Silver = 107.2.

This method is seen to have only a very limited application, but, when the proportion of Silver to Chlorine in Silver Chloride is ascertained, as above shewn, its application can be extended to include nearly all the metals by the following process.

All the metals, except Silver, Lead and Mercury, form Chlorides, which are soluble in water, and, if a weighed amount of any of these Chlorides is taken and dissolved in water, the

whole of the Chlorine present in it can be precipitated as Silver Chloride by the addition of excess of a solution of Silver Nitrate. This precipitate can be filtered, dried and weighed, and the weight of Chlorine in it calculated from the known relation between Silver and Chlorine, and from this weight of Chlorine the equivalent of the metal is not difficult to determine. An example will make the method of calculation clear.

Example. 1.4 grams of Potassium Chloride were dissolved in water, excess of Silver Nitrate added, and the resultant precipitate of Silver Chloride, on drying and weighing, was found to be 2.7 grams. Given the equivalent weights of Silver and Chlorine to be 108 and 35.5 respectively, find that of Potassium.

The proportion of Silver to Chlorine in Silver Chloride is 108 : 35.5.

Hence 2.7 grams of Silver Chloride contain $2.7 \times \frac{35.5}{143.5} = .668$ gram of Chlorine.

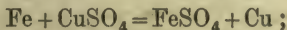
Hence, in Potassium Chloride, .668 gram of Chlorine is combined with $1.4 - .668 = .732$ gram of Potassium.

Therefore 35.5 grams of Chlorine would combine with $35.5 \times \frac{.732}{.668} = 38.9$ grams of Potassium.

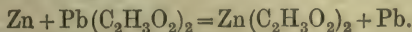
Therefore the equivalent weight of Potassium is 38.9.

Method V. Equivalents by Displacement. Certain metals, when placed in the solutions of Salts of other metals, will turn out an equivalent weight of the dissolved metal from the Salt, themselves passing into solution.

Thus, when Iron is placed in a solution of Copper Sulphate, Iron Sulphate is left in the solution and metallic Copper is deposited.



or, again, if Zinc is placed in a solution of Lead Acetate, the Zinc passes into solution and Lead is deposited.



Now, if the equivalent weight of one of the metals is known, that of the other can be calculated by observing the weights of the original metal used and of the metal deposited.

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Example. .72 gram of Zinc was placed in a solution of Lead Acetate; the Lead deposited, having been washed and dried, was found to weigh 2.29 grams. If the equivalent weight of Zinc is 32.5, find that of Lead.

Since .72 gram of Zinc displaces 2.29 grams of Lead, 32.5 grams of Zinc would displace $2.29 \times \frac{32.5}{.72} = 103.4$ grams of Lead.

Therefore the equivalent weight of Lead is 103.4.

Method VI. Equivalents by Electrolysis. When solutions of salts of two different metals are subjected to Electrolysis and the same current passes through both electrolytic cells, the weights of the two metals liberated at the Kathode plates are proportional to the equivalents of the metals, and, if the liberated metals do not attack water, the increase in weight of the Kathode plates can be easily ascertained. Then, if the equivalent of one of the metals is known, that of the other is easily calculated from these weights.

Example. Two cells, containing respectively Copper Sulphate solution and Lead Acetate solution, with plates of Copper and Lead, were subjected to the same current for some time. The Kathode Copper plate increased by .138 gram and the Kathode Lead plate by .453 gram. If the equivalent of Copper is 31.5, find that of Lead.

Since the weights .138 of Copper and .453 of Lead are proportional to their equivalent weights, the equivalent of Lead = $\frac{.453}{.138} \times 31.5 = 103.4$.

ATOMIC WEIGHT.

The Atomic Weight of an element is the least weight of that element found in the molecule of any of its compounds.

It represents, as its name implies, the weight of one atom of the element, that of Hydrogen being taken as the standard and equal to unity.

Its relation to the Equivalent or Combining Weight of the element is shewn thus:—

If one atom of Hydrogen combines with (or replaces) one

atom of the element, as is supposed to be the case in the compounds HCl and NaCl , then the Atomic Weights of Chlorine and Sodium are equal to their Equivalent Weights.

If two atoms of Hydrogen combine with (or replace) one atom of the element, as in the compounds H_2O and CuO , then the Atomic Weights of Oxygen and Copper are twice their Equivalent Weights.

Similarly, it can be seen from the compounds Ammonia NH_3 and Methane CH_4 that the Atomic Weights of Nitrogen and Carbon are 3 times and 4 times their Equivalent Weights respectively.

It would seem, then, that the Atomic Weights of the elements are determined by multiplying their Equivalent Weights by some small whole number, 1, 2, 3 or 4. This whole number is called the *Valency* of the element.

The *Valency* of an element is defined as the number of atoms of Hydrogen which one atom of the element combines with or replaces.

Hence Atomic Weight = Equivalent \times Valency, and if the Equivalent of an element has been determined by one of the methods described above, the Atomic Weight must be this Equivalent multiplied by 1, 2, 3 or 4.

The Valency of an element, if it is a non-metal, is seen in the compound it forms with Hydrogen; thus Sulphur, as seen in Sulphuretted Hydrogen, H_2S , is di-valent. Nitrogen in Ammonia, NH_3 , is tri-valent.

When the element is a metal, and forms no compound with Hydrogen, its valency is best shewn in its Chloride; thus Sodium in NaCl is clearly mono-valent, Antimony in SbCl_3 is tri-valent and Tin in SnCl_4 is tetra-valent.

Several elements possess two (and possibly even more) valencies, forming two sets of compounds with their different powers of replacing Hydrogen.

For instance, Copper in its Cuprous Salts Cu_2O , CuCl , is mono-valent; but, in its Cupric salts CuO , CuCl_2 , it is di-valent; similarly, Iron is di-valent in the Ferrous salts FeO , FeCl_2 , and tri-valent in the Ferric salts Fe_2O_3 , FeCl_3 .

To return to the definition that the Atomic Weight of an element is the *least* weight of it found in the molecule of any of its compounds. Suppose, for a moment, that the substance Benzene was the simplest compound of Hydrogen and Carbon known. The weight of its molecule—determined by methods which will be discussed later—is found to be 78, of which, by analysis, 72 parts are known to be Carbon and 6 parts Hydrogen.

Its formula, on the supposition that no simpler compound containing Carbon was known, would be written CH_6 , and the Atomic Weight of Carbon would be 72.

Now, suppose that, later, such a compound as Propane was discovered, with a molecular weight of 44 and containing 36 parts of Carbon and 8 of Hydrogen.

This discovery would alter the previous idea of the Atomic Weight of Carbon; it would have to be lowered to 36; the formula of Propane would be written CH_8 and that of Benzene C_2H_6 .

Again, suppose that, next, the compound Methane was discovered with a molecular weight of 16, of which 12 was Carbon and 4 Hydrogen.

This would entail a further reduction in the Atomic Weight of Carbon down to 12; the formula of Methane would be written CH_4 , while those of Propane and Benzene would be C_3H_8 and C_6H_6 respectively.

This is, indeed, the present state of affairs, but, if, presently, some compound of Carbon is discovered containing only 6 parts of Carbon in its molecule, an alteration of the present Atomic Weight from 12 to 6 would be necessary, and a doubling of the number of Carbon atoms at present supposed to exist in the molecules of all its compounds would have to take place.

Law of Dulong and Petit. Early in the nineteenth century an important observation was made by Dulong and Petit concerning the relation between the Atomic Weights of the elements, which had been discovered up to that time, and their Specific Heats.

They noticed that the larger the Atomic Weight of an element the smaller its Specific Heat, and that the products

obtained by multiplying the two together formed numbers which, for the different elements, were approximately constant, being in the neighbourhood of 6.3.

To this product the name of Atomic Heat has been given, and it follows that, if

$$\text{Atomic Weight} \times \text{Specific Heat} = \text{Atomic Heat (6.3),}$$

$$\text{then, Atomic Weight} = \frac{6.3}{\text{Specific Heat}}.$$

A few Atomic Heats are given in the table below :

Element.	Specific Heat.	Atomic Weight.	Atomic Heat.
Iron - - - -	.112	56	6.3
Copper - - - -	.095	63	6.0
Tin - - - -	.055	118	6.5
Sodium - - - -	.29	23	6.7
Potassium - - - -	.166	39	6.5
Carbon } at 200° C.	.273	12	3.2 }
(Diamond) } at 1000° C.	.459	12	5.5 }
Silicon - - - -	.177	28	4.95

It will be noticed that the Atomic Heats of the various elements are by no means accurately constant, and that the variation in the case of Carbon and Silicon is considerable, though it approximates more to 6.3 as the temperature rises.

This Law is therefore not at all an *accurate* method for finding Atomic Weights, but serves only for giving approximate values.

It is, however, of great use, once the Equivalent of a metal has been accurately determined, for the Atomic Weights calculated by its help are sufficiently approximate to decide which of the multiples of the Equivalent (1, 2, 3 or 4) is to be used to give the accurate Atomic Weight.

Example. The Equivalent of Copper is 31.51, and its Specific Heat is .095. What is its Atomic Weight ?

By dividing the Atomic Heat 6.3 by .095 the number 66.3 is obtained as an approximate Atomic Weight, and clearly the multiple of 31.51 which comes nearest to this number is 31.51×2 . Hence the accurate Atomic Weight of Copper is

$$31.51 \times 2 = 63.02.$$

Isomorphism. Mitscherlich (1818) noticed that the crystals of the Arsenates and Phosphates of Potassium and Ammonium were so like each other as to be quite indistinguishable even on close inspection. From the observance of this and other cases he put forward the following conclusions :

- (1) That bodies of different chemical composition may have the same crystalline form.
- (2) That bodies of similar chemical constitution have the same crystalline form.

He embodied these two statements in a law.

Mitscherlich's Law. *The same number of atoms combined together in the same manner produce the same crystalline form ; this form is independent of the chemical nature of the atoms, and is determined solely by their number and mode of combination.*

This phenomenon is called *Isomorphism*. Examples of it are seen in the mineral Carbonates, Calcite, CaCO_3 , Dolomite, $(\text{MgCa})\text{CO}_3$, Chalybite, FeCO_3 , and Diallogite, MnCO_3 , which all have similar rhombohedral crystals.

The Alums all crystallize in octohedra, and have a general formula, which may be expressed R_2SO_4 , $\text{M}_2(\text{SO}_4)_3$, $24\text{H}_2\text{O}$, where R may be any of the mono-valent metals Sodium, Potassium, Rubidium, Silver or Ammonium, and M any of the tri-valent metals Aluminium, Iron, Chromium or Manganese.

Thus ordinary Alum is K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, $24\text{H}_2\text{O}$, and Chrome Alum is K_2SO_4 , $\text{Cr}_2(\text{SO}_4)_3$, $24\text{H}_2\text{O}$.

When isomorphous substances dissolve in water, if a crystal of one of the forms is suspended in a saturated solution of any other of the forms, it will continue to grow, remaining perfect in shape, and forming what is called an "*overgrowth*." For instance, if a dark violet crystal of Chrome Alum is suspended in a saturated solution of Potash Alum, a colourless over-

growth is formed, and the dark crystal of Chrome Alum can still be seen in the interior.

This Law of Mitscherlich has been of considerable use in the determination of Atomic Weights. By means of it Mitscherlich was able to fix the Atomic Weight of Selenium, because he found that the Sulphates and Selenates of Potassium were isomorphous.

Analyses of these two compounds gave :

	K	O	S	Se
Potassium Sulphate	- 44.83	36.78	18.39	—
Potassium Selenate	- 44.83	36.78	—	45.40

Since, from the Law, the number of atoms of Sulphur and Selenium present in a molecule of each of these compounds must be the same, their Atomic Weights must be proportional to the two numbers 18.39 and 45.40 respectively. Given the Atomic Weight of Sulphur as 32, that of Selenium must be

$$32 \times \frac{45.40}{18.39} = 79.$$

Again, in 1836, the Atomic Weight of Copper was supposed to be 63, and that of Silver 216, and their native Sulphides were represented by the formulae Cu_2S and AgS respectively. It was then pointed out that these minerals were isomorphous, and hence their constitution must be the same.

This caused the formula for Silver Sulphide to be altered to Ag_2S , and the Atomic Weight of Silver became 108, a number which agreed with subsequent determinations of it.

The Law of Mitscherlich has also served a useful purpose in fixing the composition of the mineral Magnetite. By analysis, the formula Fe_3O_4 is assigned to it. Now this mineral is a member of the isomorphous group of minerals called the Spinel group. Examples of this group are Gahnite, $\text{ZnO} \cdot \text{Al}_2\text{O}_3$, Chromite, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and Spinel, $\text{MgO} \cdot \text{Al}_2\text{O}_3$. All these, it will be noticed, consist of a di-valent Oxide united with a tri-valent Oxide, and hence Magnetite must be a compound of the two Oxides of Iron, Ferrous Oxide, FeO , and Ferric Oxide, Fe_2O_3 , a conclusion not easily reached by other methods.

Periodic Law. About the year 1870, it was independently discovered by Mendeléeff and Lothar Meyer that, when the elements were arranged in the order of their Atomic Weights, a similarity in their properties recurred after an interval of about 7 or 8 elements, that is, the properties and compounds of Nos. 2, 9, 16, etc., were similar, as also were those of Nos. 3, 10, 17, etc., or Nos. 7, 14, 21. This is best explained by a reference to the table (Fig. 39), which is similarly arranged to that of Mendeléeff's original table, with the addition of elements discovered since his time.

It will be noticed that there are several gaps in the sequence, notably in the elements of high Atomic Weight, but there were more gaps in Mendeléeff's original table. Two of these are now occupied by the elements Scandium and Germanium, and it is noteworthy that, fifteen years before they were discovered, Mendeléeff, from the fact that these gaps were present, predicted their discovery, and also many facts about their properties and those of their compounds. He called them Eka-Boron (now Scandium), and Eka-Silicon (now Germanium), and these predictions were most accurately fulfilled when the elements were discovered and their properties and compounds investigated.

These extraordinary prophecies naturally drew the attention of the scientific world to the Periodic classification of elements, and gave it, for a time, an importance far beyond its real value; and until fresh facts are discovered in the relationships between one element and another, the student should not insist too closely on the near relationship between one element and another because they happen to fall in the same Group.

PROBLEMS.

17. .54 gram of Zinc, placed in dilute Sulphuric acid, liberated 185 c.c. of Hydrogen gas measured at 0° C. and 760 mm. Calculate the Equivalent Weight of Zinc.

18. .35 gram of Magnesium in dilute Hydrochloric acid yielded at 10° C. and 775 mm. 343 c.c. of Hydrogen gas. Calculate the Equivalent Weight of Magnesium.

THE PERIODIC SERIES OF THE ELEMENTS.

Series	Group 0.	Group I. R_2O	Group II. RO	Group III. R_2O_3	Group IV. $RH_4 RO_2$	Group V. $RH_3 R_2O_5$	Group VI. $RH_2 RO_3$	Group VII. $RH R_2O_7$	Transition elements
1.		H 1·008							
2.	He 3·99	Li 6·94	Be 9·1	B 11·0	C 12·0	N 14·01	O 16·0	F 19·0	
3.	Ne 20·2	Na 23·0	Mg 24·32	Al 27·1	Si 28·3	P 31·04	S 32·07	Cl 35·46	
4.	A 39·88	K 39·1	Ca 40·07	Sc 44·1	Ti 48·1	V 51·0	Cr 52·0	Mn 54·93	{ Fe 55·84 Co 58·97 Ni 58·68
5.	—	63·57 Cu	65·37 Zn	69·9 Ga	72·5 Ge	74·96 As	79·2 Se	79·92 Br	
6.	Kr 82·92	Rb 85·45	Sr 87·63	Yt 89·0	Zr 90·6	Nb 93·5	Mo 96·0	—	{ Ru 101·7 Rh 102·9 Pd 106·7
7.	—	107·88 Ag	112·40 Cd	114·8 In	119·0 Sn	120·2 Sb	127·5 Te	126·92 I	
8.	Xe 130·2	Cs 132·81	Ba 137·37	La 139·0	Ce 140·25	—	—	—	?
9.	—	—	—	—	—	—	—	—	
10.	—	—	—	Yb 172·0	—	Ta 181·0	W 184·0	—	{ Os 190·9 Ir 193·1 Pt 195·2
11.	—	197·2 Au	200·6 Hg	204·0 Tl	207·1 Pb	208·0 Bi	—	—	
12.	Nt 222·5	—	Ra 226·4	—	Th 232·4	—	U 238·5	—	

FIG. 39.

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19. 31 gram of Aluminium, when boiled with a strong solution of Caustic Soda, evolved 415 c.c. of Hydrogen gas, measured over water at 14° C. and 745 mm. Calculate the Equivalent Weight of Aluminium.

20. 42 gram of Sodium, when placed in Methylated Spirits, gave off 225 c.c. of Hydrogen gas at 10° C. and 750 mm. (The Vapour Pressure of Methylated Spirits may be taken as four times that of water.) Calculate the Equivalent Weight of Sodium.

21. Pure dry Oxygen gas was passed over .154 gram of Diamond dust heated to redness, the resulting gases were led through a solution of Caustic Potash, which increased in weight by .565 gram during the operation. Calculate the Equivalent Weight of Carbon.

22. .52 gram of Tin, treated with strong Nitric acid, and the residue evaporated and heated to redness, yielded .66 gram of Stannic Oxide. Calculate the Equivalent Weight of Tin.

23. .422 gram of Copper yielded on complete oxidation .529 gram of black Copper Oxide.

.567 gram of red Copper Oxide yielded on reduction by Hydrogen .503 gram of Copper.

Calculate the Equivalent Weights of Copper for the two cases and comment on the results obtained.

24. One gram of a metallic Chloride yielded, on reduction by Hydrogen, .496 gram of metal. Calculate the Equivalent Weight of the metal.

25. .5 gram of Magnalium (an alloy of Magnesium and Aluminium), placed in dilute Hydrochloric acid, yielded 556 c.c. of Hydrogen gas at 0° C. and 760 mm. If the Equivalent Weights of Magnesium and Aluminium are 12 and 9 respectively, calculate the percentage of Magnesium in Magnalium.

26. 42 gram of Zinc was placed in a solution of Lead Acetate, and it was found that 1.34 grams of Lead were deposited. Given the Equivalent Weight of Zinc as 32.5, find that of Lead.

27. 1.19 grams of Tin yielded, on complete oxidation, 1.51 grams of Tin Oxide. The Specific Heat of Tin is .054; find its accurate Atomic Weight.

28. The Chloride of a tri-valent element contains 80 per cent. of Chlorine; find the Atomic Weight of the element.

29. 4.258 grams of the Chloride of a metal yielded 5.869 grams of Silver Chloride when precipitated with Silver Nitrate. If the equivalent Weight of Silver is 108 and that of Chlorine is 35.5, find that of the metal.

30. .3 gram of a metal R evolved 388 c.c. of Hydrogen gas collected over water at 6° C. and 766 mm. when placed in Hydrochloric acid. The Specific Heat of R is .22; calculate its Equivalent and Atomic Weights, and give the formula of its Chloride.

31. 10.358 grams of crystallized Borax yield 5.478 grams of anhydrous Borax on drying. Assuming that the formula of the crystalline salt is $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and given that the Atomic Weights of Sodium and Oxygen are 23 and 16 respectively, find the Atomic Weight of Boron.

32. .78 gram of a liquid Chloride of Phosphorus were decomposed by water, Silver Nitrate was added, and the dried precipitate of Silver Chloride was found to weigh 2.441 grams. Calculate the Equivalent Weight of Phosphorus, given those of Silver and Chlorine to be 108 and 35.5 respectively.

PRACTICAL EXERCISES.

To find the Equivalent Weight of Magnesium by Displacement of Hydrogen from an Acid. Clean a piece of Magnesium wire or ribbon with sandpaper and weigh it carefully. The amount taken depends on the size of the graduated cylinder to be used. Take a little less than .1 gram of Magnesium for every 100 c.c. in the cylinder. Fill the graduated cylinder with dilute acid—Hydrochloric acid is the best to use—and invert it in a small pneumatic trough also containing dilute acid.

Place the Magnesium in a small test tube, fill up the tube with water, and insert it under the open end of the cylinder.

When all action has ceased and the Magnesium has all dissolved, transfer the cylinder to a deep vessel containing water, make the levels inside and outside the cylinder equal, and read the volume of Hydrogen.

Correct this volume for temperature and pressure, allowing for the pressure of the aqueous vapour, and calculate the equivalent of Magnesium as indicated on pages 125-6.

The equivalents of Zinc, Iron and Aluminium may be determined in a precisely similar manner. The action in the case of Aluminium is usually very slow, but may be quickened by adding a few drops of a solution of Platinum Chloride to the acid.

For Zinc use .25 gram, for Iron .2 gram and for Aluminium .07 of a gram per 100 c.c. volume of the graduated cylinder.

To find the Equivalent of Sodium. Sodium is made to displace Hydrogen from Methylated Spirits, as the action is less violent than in the case of water. The apparatus shewn

in the figure (Fig. 40) should be used. The tube *A* contains the weighed piece of Sodium, *B* is a joint of rubber gas-tubing, *C* is a bent glass tube of fairly wide bore passing under the graduated cylinder. By slightly raising *A*, the Sodium is caused to slide down through *B* and *C*, and at once rises up through the spirit in the cylinder.

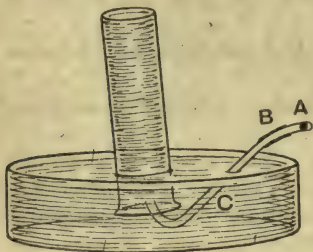


FIG. 40.

The Sodium must be cut and weighed as rapidly as possible just before being used. It is best to weigh the tube *A* empty, with a cork, then put the Sodium in it, cork the tube, and weigh again. Take .2 gram for a 100 c.c. cylinder.

Calculate as before, but take the pressure of the vapour of Methylated Spirits to be four times that of water at the same temperature.

The equivalent of Calcium may be determined in the same manner, using Water instead of Methylated Spirits.

To find the Equivalent of Tin. Carefully weigh a small porcelain crucible with its lid. Introduce about .5 gram of pure granulated Tin, and weigh again.

Take a piece of glass tube about 6 in. long, and draw out a jet at one end. Dip this jet into strong Nitric acid, and place your finger over the other end. Now put the lid on the crucible, raise it slightly at one side, insert your glass tube, and allow one or two drops of acid to fall on the Tin. Close the lid, wait a minute or so, and repeat the process. After a time the addition of more acid causes no further action. Heat the crucible carefully till the contents are dry; then heat it very strongly for some time, say ten minutes. When cold, weigh it again. The Tin is converted into Tin Oxide, and the increase in weight is the weight of the Oxygen.

From the observed weights calculate the weight of Tin which combines with 8 grams of Oxygen.

The equivalents of Copper, Magnesium and several other metals may be determined in a similar manner.

To find the Equivalent of Nickel. Weigh a short piece of hard glass tubing, put in it about 1 gram of Nickel Oxide and weigh again. Reduce the Oxide to metallic Nickel by heating the tube and passing Hydrogen or Coal gas through it. When cold, weigh again, and the loss in weight gives the weight of the Oxygen.

Calculate the weight of Nickel which combines with 8 grams of Oxygen.

The equivalents of many metals may be found by reducing their Oxides in this way.

To find the Equivalent of Silver. Take a known weight of powdered Silver in a hard glass tube, heat it gently and pass Chlorine gas slowly over it for some time. When combination ceases, allow the tube to cool and weigh it again. The increase is the weight of Chlorine which has combined with the Silver.

Calculate the weight of Silver which combines with 35.5 grams of Chlorine.

To find the Equivalent of Potassium. Weigh out about .5 gram of pure dry Potassic Chloride. Dissolve it in a small quantity of distilled water, and add to it excess of Silver Nitrate solution. All the Chlorine in the Potassic Chloride is precipitated as Silver Chloride. Filter the liquid through a filter paper, of which the weight of the ash is known. Wash the precipitate well with distilled water and dry it on a cone over a sand bath. During filtering and drying, the precipitate should be shielded from light as much as possible.

When the precipitate is dry, transfer as much of it as possible to a weighed porcelain crucible, fold up the filter paper and wrap it round with a piece of Platinum wire. Burn the paper thoroughly in a bunsen flame, and allow the ash to fall into the porcelain crucible which contains the precipitate.

Add two or three drops of strong Hydrochloric acid to the contents of the crucible, put on the lid, and heat it for five minutes in a bunsen flame.

Weigh when cool, subtract from this weight the weights of the empty crucible and of the ash of the filter paper, and the result is the weight of Silver Chloride in the crucible.

Calculate the equivalent of Potassium as indicated on page 129.

To find the Equivalent of Zinc, by causing it to displace Copper from a solution of Copper Sulphate. Weigh a small porcelain dish, and then place in it about .8 gram of clean Zinc foil. Weigh again.

Half fill the dish with a solution of Copper Sulphate, and stir with a glass rod, warming slightly to accelerate the action. If the solution loses its colour, add more. When the Zinc seems to have all disappeared, allow the Copper to settle, and carefully suck off as much liquid as possible with a pipette. Wash the Copper three or four times, using a wash-bottle and sucking off the liquid as before. Wash the stirring-rod into the dish. Now wash twice with a little Alcohol, and drain off. Dry the Copper in the dish over a sand bath, being careful not to overheat it: and when cold, weigh again.

Calculate the equivalent of Zinc, given that of Copper to be 31.5.

To find the Equivalent of Sodium by a Volumetric Method. Weigh out quickly about .5 gram of clean Sodium. Dissolve it in 50 c.c. of distilled water. Add a few drops of litmus solution and titrate the liquid with N. HCl.

Calculate the equivalent of Sodium on the assumption that every c.c. of N. HCl added is equivalent to .001 gram of Hydrogen.

The equivalent of Calcium may be determined in a similar manner.

To find the Equivalent of Magnesium by a Volumetric Method. Weigh out not more than .2 gram of Magnesium wire. Dissolve it in 25 c.c. of N. HCl, and determine the volume of unneutralized acid by titration with N. KOH.

Calculate the equivalent of Magnesium, as described above for Sodium, from the quantity of N. HCl neutralized by the metal.

CHAPTER XIII.

VAPOUR DENSITY AND MOLECULAR WEIGHT.

THE *Density* of a gas or vapour is usually referred to that of Hydrogen as unit, and is defined as the number of times a given volume of the gas or vapour is heavier than the same volume of Hydrogen, both being measured at the same temperature and pressure.

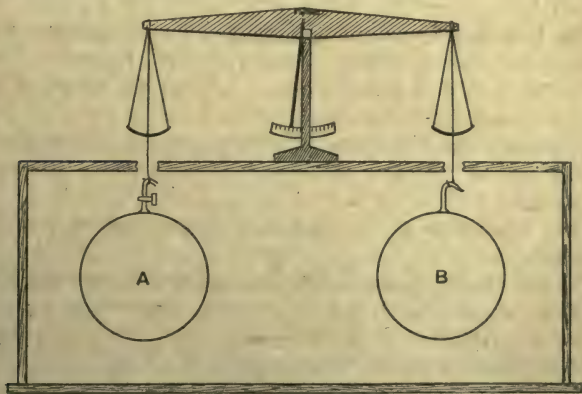


FIG. 41.—Measurement of the Density of a Gas.

Its accurate determination is of very great importance, and one or two of the principal methods of determining it are appended.

I. When the Substance is a Gas at Ordinary Temperatures.
A large glass globe *A* (Fig. 41), of known volume, is suspended

from one arm of a balance, and a similar globe *B*, of approximately the same volume, is suspended from the other arm of the balance, so as to eliminate corrections for the buoyancy of the air. The globes are kept in a closed box underneath the balance during weighings to avoid air currents.

The globe *A* is exhausted as fully as possible by a Sprengel air pump and weighed. The gas under consideration is then allowed to enter, and the increase in weight noted. This experiment, repeated two or three times, gives sufficient accuracy on a mean of the results being taken.

If, now, Hydrogen gas is admitted to *A* in a similar manner, and under the same conditions as to temperature and pressure, the weights of the two equal volumes of the gases can be compared, and the density of the gas determined directly.

Or, the known volume of *A* can be corrected for temperature and pressure, and the result compared with the weight of the same volume of Hydrogen at normal temperature and pressure, taking 1 litre of Hydrogen as weighing .09 gram under normal conditions.

II. When the Substance, whether Solid or Liquid, can be vaporized without Decomposition. Two methods are in common use; one is due to Victor Meyer and the other to Dumas.

Victor Meyer's method. This method consists in introducing a small quantity of the solid or liquid under consideration into a weighed stoppered glass tube, seen enlarged in the diagram (Fig. 42), and obtaining its exact weight. Meanwhile the glass apparatus is thoroughly dried by blowing hot air through *A*, and has its bulb immersed in a liquid whose Boiling Point is some 20° C. or 30° C. higher than the Boiling Point of the substance under investigation. This liquid is kept steadily boiling for 15 minutes, till expansion of the contained air has ceased, and the whole apparatus has attained a constant temperature.

The small weighed tube is then introduced at the top of the apparatus *B*, which is promptly corked, and the graduated tube *C* placed in position over the delivery tube. A small

quantity of glass wool or sand is placed at the bottom of *A* to break the fall of the small glass tube.

The high temperature of the bath very soon causes the solid or liquid to vaporize; the cork is blown out of the small glass tube, and the vapour formed drives out an equivalent quantity of air into the graduated tube *C*. This air is allowed to attain the temperature of the surrounding atmosphere, the water levels inside and outside the tube are made equal, and its volume is accurately read, as is also the pressure and temperature obtaining at the time of the experiment.

Since hot air, at the temperature of the interior of the bulb, has been driven out by the vapour of the substance under examination, and this hot air has cooled down to ordinary temperatures, its volume represents the volume which the vapour itself would occupy, if it could be obtained as vapour, at ordinary room temperature, and so, if its weight is compared with that of an equal volume of Hydrogen, at the same temperature and pressure, the vapour density of the substance is obtained.

An example will shew the method of calculation.

Weight of liquid vaporized	-	-	-	·18 gram.
Volume of air driven out	-	-	-	37·5 c.c.
Pressure 763 mm., Temperature	-	-	-	14° C.
Vapour pressure of water at 14° C.	-	-	-	12 mm.

o.c.

K

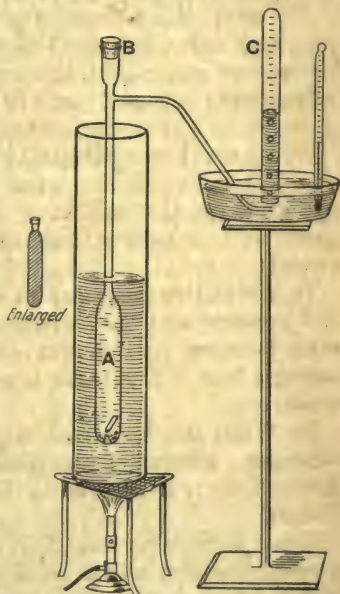


FIG. 42.—Victor Meyer method for determining Vapour Densities.

Volume of air driven out corrected to 0° C. and 760 mm.

$$= 37.5 \times \frac{763 - 12}{760} \times \frac{273}{287} = 35.25 \text{ c.c.}$$

Weight of 35.25 c.c. of Hydrogen at 0° C. and 760 mm.

$$= 35.25 \times .00009 = .0031725 \text{ gram.}$$

$$\text{Hence the vapour density of liquid} = \frac{.18}{.0031725} = 56.75.$$

Water is the liquid usually employed in the outer vessel in Victor Meyer's apparatus, but, if a temperature higher than 100° C. is required to vaporize the liquid (or solid) substance whose vapour density is required, Acetic acid (Boiling Point 119° C.) or Aniline (Boiling Point 180° C.) may be used.

It is not at all necessary to know the exact temperature of the liquid bath, all that is required being that this temperature shall be constant during the operation. This is the great value of this method, as the accurate reading of a high temperature is unnecessary, but its application is unfortunately limited, in practice, to temperatures below 200° C., and many substances are not vaporized till a much higher temperature is reached. For such substances, Dumas' method is used; its application is practically unlimited as to temperature, but the temperature of the vapour itself must be known with accuracy, a matter of some difficulty with high temperatures.

Dumas' method. In this process a large light glass bulb of capacity 200 to 300 c.c. is usually employed. This is weighed full of air, and then 7 or 8 grams of the volatile substance are placed in it. The bulb and its contents are then placed in a bath (Fig. 43) of a liquid with a constant Boiling Point some 30° C. or 40° C. above that of the substance in the bulb, and kept there till the vapour ceases to issue from the narrow tip of the tube. It is then assumed that the vapour has driven all the air out of the bulb, which now, therefore, contains only the vapour of the substance employed. The tip of the glass tube is then sealed up with a blowpipe and, at the same time, the temperature of the bath is taken as accurately as possible.

The bulb is next removed from the bath, dried and weighed. It is then placed in a deep vessel full of cold water, and the tip of the glass tube is broken off, when, if the experiment has been successful, and all the air was driven out of the bulb, water will enter until it is completely full, owing to the vapour condensing back again to its original state.

By weighing it when full of water and subtracting the weight of the bulb full of air, the weight of the water in the bulb is obtained, and this gives, with fair accuracy, its volume in c.c.

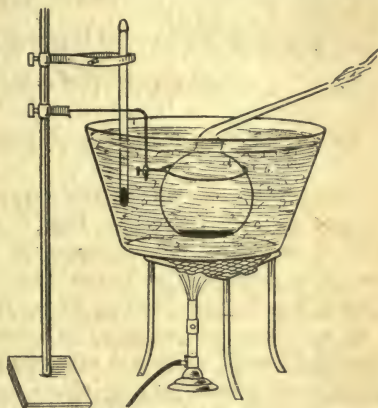


FIG. 43.—Dumas' method for determining Vapour Densities.

The next step is to calculate the weight of this volume of air at the temperature and pressure at which the bulb was first weighed. This weight of air, if subtracted from the weight of the bulb full of air, gives the weight of the bulb when vacuous, and hence the weight of the vapour which fills it at the temperature of the bath can be obtained by subtracting the weight of the vacuous bulb from the final weight of the bulb and its contained vapour.

On comparing this weight with the weight of a similar volume of Hydrogen under the same conditions, the vapour density of the substance under examination can be calculated.

Example.

Weight of bulb full of air at 12°C . and 740 mm.

= 27.36 grams.

Weight of bulb full of vapour at 99°C . and 740 mm.

= 27.69 grams.

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Weight of bulb full of water = 239.86 grams.

Hence the volume of the bulb is approximately

$$239.86 - 27.36 = 212.5 \text{ c.c.}$$

Since 1 c.c. of Air at 0° C. and 760 mm. weighs .001293 gram, the weight of Air which fills the bulb at 12° C. and 740 mm.

$$= 212.5 \times \frac{273}{285} \times \frac{740}{760} \times .001293 = .256 \text{ grams.}$$

From which the weight of the vacuous bulb

$$= 27.36 - .256 = 27.104 \text{ grams.}$$

Hence weight of vapour in the bulb at 99° C. and 740 mm.

$$= 27.69 - 27.104 = .586 \text{ gram,}$$

i.e. 212.5 c.c. of vapour at 99° C. and 740 mm. weigh .586 gram ;

i.e. $212.5 \times \frac{273}{372} \times \frac{740}{760}$ c.c. of vapour at 0° C. and 760 mm. weigh .586 gram ;

∴ 1 c.c. of vapour at 0° C. and 760 mm. weighs

$$\frac{.586 \times 372 \times 760}{212.5 \times 273 \times 740} \text{ grams.}$$

But 1 c.c. of Hydrogen at 0° C. and 760 mm. weighs .00009 gram ;

∴ Vapour Density of Substance

$$\begin{aligned} &= \frac{.586 \times 372 \times 760}{212.5 \times 273 \times 740 \times .00009} \\ &= 42.88. \end{aligned}$$

One great objection to this method is that a large amount of the substance is needed to make sure of driving all the air out of the bulb. It possesses, however, distinct advantages in that, by using porcelain bulbs, the vapour densities of substances at high temperatures, such as 1000° C., can be obtained, such high temperatures being measured with a Platinum resistance thermometer.

By an investigation of this nature it was discovered that the molecule of Iodine, which at lower temperatures contains two atoms, at temperatures above 1000°C ., contains only one atom, and a similar decrease in the number of atoms of Sulphur in its molecule from S_8 to S_2 was observed in this way.

It has already been noticed, p. 121, that the molecule of Hydrogen gas contains two atoms, hence its Molecular Weight is 2. Now the Vapour Density of a substance represents the number of times it is heavier than Hydrogen, and since, by Avogadro's Law, equal volumes of all gases contain an equal number of molecules, it follows that the Vapour Density represents the number of times one molecule of a gas is heavier than one molecule of Hydrogen. This, it has been noticed above, has a molecular weight of 2; therefore the Molecular Weight of any substance is obtained by multiplying its Vapour Density by 2;

i.e. Molecular Weight = Vapour Density \times 2,

or Vapour Density = $\frac{\text{Molecular Weight}}{2}$.

Hence the determination of the Vapour Density of a substance is of great use in obtaining a value for the Molecular Weight of that substance.

Since a comparatively small number, of Inorganic compounds at any rate, is vaporizable without decomposition, these methods of Dumas and Victor Meyer have only a limited application, and other means must be found for the determination of the Molecular Weights of compounds which are not vaporizable. Some of the methods are described below.

(1) *The Raising of the Boiling Points of Solutions.* When any soluble substance is present in a solvent, the Boiling Point of the solution is higher than that of the pure solvent, and it has been shewn that, for dilute solutions, the raising of the Boiling Point is directly proportional to the weight of the solute in a given weight of solvent.

This means that, if 1 gram of a substance dissolved in 100 grams of solvent raises the Boiling Point 0.05°C ., then

2 grams of the same substance dissolved in the same weight of the solvent will raise the Boiling Point 10°C .

Raoult (1883) put forward his Law on this point, that "an equal number of Molecular Weights of different solutes in the same quantity of solvent give the same elevation of the Boiling Point."

Raoult's Law may be conveniently stated thus :

"The rise in temperature of the Boiling Point of a solvent is proportional to the number of molecules of the solute in the solution, and inversely proportional to the Molecular Weight of the solute."

Thus one Molecular Weight in grams of Sugar (342 grams), or Aniline (93 grams), dissolved in 100 grams of water, raises its Boiling Point from 100°C . to 105.2°C . This rise of 5.2°C . is called the *boiling constant* for water.

Every solvent has its boiling constant, that of Benzene being 26.7°C ., of Ether 21.6°C . and of Carbon Disulphide 23.5°C .

Suppose, for example, w grams of a substance, of Molecular Weight M , dissolved in 100 grams of water, raised its Boiling Point $x^{\circ}\text{C}$. then the following relation holds good :

$$\frac{w}{M} = \frac{x}{5.2},$$

$$\text{or } M = \frac{5.2 \times w}{x},$$

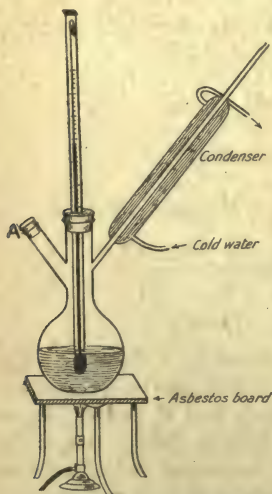


FIG. 44.—Determination of Molecular Weights by the raising of the Boiling Points of solutions.

and this relation is of great value in determining the Molecular Weights of many substances.

In practice, an apparatus similar to the one shewn in the diagram (Fig. 44) is used.

A known weight—about 50 grams—of the solvent is introduced into the flask, and its Boiling Point accurately determined

by means of the Beckmann thermometer to the nearest hundredth of a degree. Then a weighed amount—1 or 2 grams—of the solute is introduced through the tube *A*, and the rise in Boiling Point is accurately noted.

The strength of the solution is kept practically constant during the operation by the condenser, which returns the condensed vapour of the solvent to the flask. It is usual to subtract .5 gram from the weight of the solvent, to allow for that portion of it condensed on the walls of the flask and in the condenser.

Example. Weight of solvent (water) in the flask 47.64 grms.
 „ solute introduced - - 3.734 „
 Rise in Boiling Point - - - .77° C.

Actual weight of solvent in use = $47.64 - .5 = 47.14$ grams.
 Strength of solution per 100 grams of solvent

$$= \frac{100 \times 3.734}{47.14} = 7.921 \text{ grams.}$$

Now the boiling constant for water is 5.2°C .

Hence 7.921 grams represents $\frac{.77}{5.2} \times \text{Molecular Weight}$;

$$\therefore \text{Molecular Weight of solute} = \frac{7.921 \times 5.2}{.77} \\ = 53.49.$$

(2) *The Lowering of the Freezing Point of a Solution.* The lowering of the Freezing Point of dilute solutions obeys precisely similar laws, with regard to the quantity and Molecular Weight of the solute, as the raising of the Boiling Point; i.e. “*The depression of the Freezing Point of a solvent is proportional to the weight of the solute in a given weight of solvent, and inversely proportional to the Molecular Weight of the solute.*”

For every solvent there is a definite “constant,” viz. the fall of the Freezing Point when 1 gram-molecular weight of the solute is dissolved in 100 grams of the solvent.

These constants are, for water 18.5°C ., for Acetic acid 39°C ., for Benzene 49°C ., etc.

It will be noted that these constants are appreciably higher than those for the rise of Boiling Point, and therefore their determination admits of a greater degree of accuracy, so that this method is the one more usually employed for Molecular

Weight determinations. The experiment is conducted in an apparatus similar to the one shewn in the diagram (Fig. 45).

Into the inner tube *A* a known weight of solvent is introduced, its Freezing Point is determined accurately by the Beckmann thermometer, the liquid being kept well stirred during the operation. The freezing mixture *F* is kept from direct contact with the vessel *A* by an annular space filled with air.

When the Freezing Point of the pure solvent has been determined, the tube *A* is taken out of the freezing mixture, the solvent melts, and then a known (small) weight of solute is introduced through the tube *B*. This is allowed to dissolve completely, and then *A* is reintroduced into the freezing mixture, and the new Freezing Point is determined.

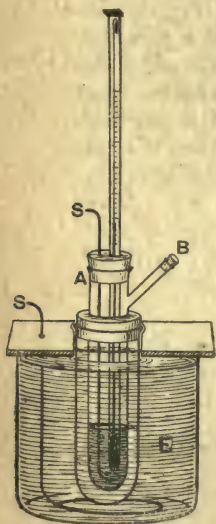


FIG. 45.—Determination of Molecular Weights by the depression of the Freezing Point of solutions.

Example. .56 gram of a solid dissolved in 40 grams of Benzene lowered its Freezing Point by 42°C . Find the Molecular Weight of the solid. Constant for Benzene is 49°C .

.56 gram of solute in 40 grams of Benzene correspond to

$$\frac{.56 \times 100}{40} = 1.4 \text{ grams in 100 grams of Benzene.}$$

1.4 grams therefore lowers the Freezing Point 42°C .

But one Molecular Weight lowers the Freezing Point 49°C .

\therefore Molecular Weight : 1.4 :: 49 : 42,

and Molecular Weight = $\frac{1.4 \times 49}{42} = 163.3$.

OSMOTIC PRESSURE.

If a dilute solution of a solid in water is placed in a thistle funnel, the head of which is covered with a tightly stretched piece of bladder, and which has a manometer (Fig. 46) fitted to the other end of the tube, then, if the funnel is placed in a vessel containing water, so that the levels inside and outside are the same, and left for a time, the manometer shortly indicates that the pressure *inside* the funnel is increasing. This goes on till a certain pressure is reached, when it remains constant, shewing that equilibrium has been established.

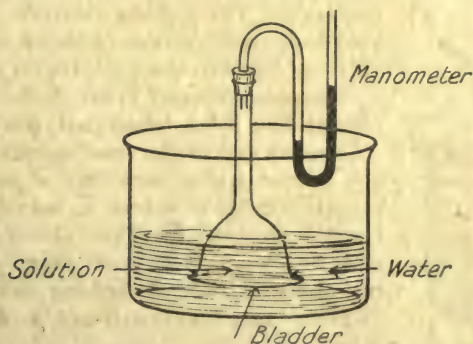


FIG. 46.—Osmotic Pressure.

The extra pressure on the solution side of the membrane which is thus exerted is called the Osmotic Pressure of the solution, and is supposed to be due to the bombarding of the membrane on that side by the molecules of the dissolved solid. These molecules pass only with the greatest difficulty through the membrane, but it allows the molecules of water to pass freely in either direction.

Animal membranes, such as the above, do not give numerically constant results, being permeable to a very varying extent by the solid molecules, but an artificial membrane has been made, which is quite impermeable to the

molecules of the solute, whilst those of the solvent pass readily through it.

This artificial membrane is made by causing Copper Ferrocyanide to be precipitated in the pores of a pot of unglazed earthenware. A dilute solution of Potassium Ferrocyanide is placed in the pot, which is immediately lowered into a dilute solution of Copper Sulphate; the two liquids meet at the centre of the walls of the pot and there deposit Copper Ferrocyanide, which serves as a perfect "semi-permeable membrane," as it is called.

Using such a membrane, very accurate determinations of the Osmotic Pressures of solutions have been made, and they are found to obey certain laws.

Law I. At constant temperature, the pressure exerted is proportional to the concentration of the solution, for the same solute.

Law II. The concentration being constant, the pressure is proportional to the absolute temperature, *i.e.* the number of degrees above -273°C .

Law III. Solutions which contain, in the same weight of solvent, equivalent proportions of the Molecular Weights of the solutes, exert equal pressures (at the same temperature).

The first two of these Laws, if closely studied, are seen to resemble Boyle's and Charles' Laws for gases. In Law I., for instance, by Boyle's Law, the pressure of a gas is proportional to the quantity of a gas present in a given space; in this Law the Osmotic Pressure is proportional to the quantity of solute present.

In Law II., Charles' Law, that the pressure of a gas is proportional to the absolute temperature, is exactly followed.

Law III. forms another method, similar to the Rise in Boiling Point and Fall in Freezing Point methods, for determining the Molecular Weight of a soluble solid, since the Osmotic Pressure is proportional to the number of Molecular Weights present in a given quantity of solvent, but, owing to the experimental difficulties in the way of the accurate measurement of Osmotic Pressure, it is a method but rarely adopted.

In the determination of Molecular Weights by any of the three last mentioned methods, in which an aqueous solution of the substance is used, it is found that certain classes of substances produce results which are quite abnormal and irregular, varying with the strengths of the solutions employed.

These abnormal results are obtained when the solutions used are those of Acids, Bases or Salts.

By these methods the Molecular Weights of such substances invariably come out too low, and, the more dilute the solution, the lower their apparent Molecular Weights, till, in nearly every case, when the solution is sufficiently dilute, the Molecular Weight obtained is found to be very approximately one half of what it ought to be.

It seems, then, that, in solution, the molecules of Acids, Bases and Salts begin to split up into two parts, each of which has its effect on the Boiling Point, Freezing Point and Osmotic Pressure of the solution, and, the more dilute the solution, the more molecules are split up, until, with sufficiently dilute solutions, all the molecules are split up into two parts, and consequently their effect is double what it ought to be.

This dissociation of the molecules of certain solutes in aqueous solution is termed Ionization, and will be more fully treated later.

PROBLEMS.

33. .062 gram of a liquid formed 23.2 c.c. of vapour at 50° C. under 720 mm. pressure. Find its Vapour Density.

(Camb. Univ. Schol. Exam.)

34. Using Victor Meyer's method, .1105 gram of a substance displaced 11.1 c.c. of air at 16° C. and 714.8 mm. Calculate the Vapour Density of the substance.

(Camb. Univ. Schol. Exam.)

35. In an experiment to find the Vapour Density of Chloroform by Victor Meyer's method, .101 gram of Chloroform displaced 20.2 c.c. of air measured over water at 16° C. under a pressure of 754 mm. Find the Vapour Density of Chloroform.

36. Using the apparatus of Victor Meyer, .15 gram of a liquid displaced 59.2 c.c. of air measured over water at 14° C. and 763 mm. By analysis, the liquid was found to contain 40 per cent. of Carbon, 6.66 per cent. of Hydrogen, and the rest was Oxygen. Find its correct formula.

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37. Find the Molecular Weight of a gas from the following data :
Volume of globe, 162.84 c.c. Temperature, 15° C. Pressure, 767.7 mm.
Weight of gas in globe, .2773 gram. (Camb. Univ. Schol. Exam.)

38. In a determination of Vapour Density by Dumas' method :

Weight of bulb full of air	-	52.346 grams.
" " vapour	-	52.170 "
Volume of bulb	-	274 c.c.
Temperature of the air	-	15° C.
" bath	-	1040° C.
Barometer	-	760 mm.

Find the Vapour Density of the compound.

39. 34 grams of a gas occupy 234 c.c. at 13° C. under a pressure of 47.5 atmospheres. Find the Density of the gas and, if possible, a molecular formula for it. The analysis shews 27.27 per cent. of Carbon and 72.72 per cent. of Oxygen. (Camb. Univ. Schol. Exam.)

40. A compound has the following percentage composition : Carbon, 40 per cent. ; Hydrogen, 6.6 per cent. ; Oxygen, 53.3 per cent. .1328 gram of it, when dissolved in 12.05 grams of water, depressed the freezing point by .35° C. If the molecular depression for water is 19° C., find the correct formula for the compound. (Camb. Univ. Schol. Exam.)

PRACTICAL EXERCISES.

To determine the Vapour Density of Chloroform by Victor Meyer's Method. The method of conducting the experiment and of making the necessary calculations is fully described on page 144. Use water as the surrounding liquid for the tube.

To determine the Vapour Density of Ether by Dumas' Method. The method is described on page 146. Use water in the bath.

To determine the Molecular Weight of Sugar by the Lowering of the Freezing Point of its Solution in Water. The method is described on page 151. Measure 20 c.c., i.e. 20 grams, of Water into the inner tube as the solvent, and add to it not more than .5 gram of Sugar.

To demonstrate Osmotic Pressure. Set up an apparatus, as described on page 153. Use a piece of pig's bladder for the membrane and a solution of Sugar in water. Fill about 10 cm. on each side of the manometer with Mercury and note the pressure after setting aside for 24 hours.

CHAPTER XIV.

THERMOCHEMISTRY.

WHENEVER, by any chemical reaction, a change, either of decomposition or combination, in the constitution of the reacting substances takes place, there is always produced simultaneously a gain or loss in that particular form of Energy which is called Chemical Energy.

Chemical Energy is Energy of the potential kind, and is due to the chemical affinity which certain elements have for certain other elements, causing them to combine, and since by the results of such combination, as, for instance, in the cylinder of a gas or petrol engine, useful work can be done, it must be a form of Energy.

Now this appearance (or disappearance) of Chemical Energy must, by the Law of the Conservation of Energy, be accompanied by the disappearance (or appearance) of a precisely equivalent quantity of Energy in another form, and this form is usually that of Heat.

To speak generally, Chemical Combination is usually accompanied by the evolution of Heat, whilst Chemical Decomposition is usually accompanied by the disappearance of Heat, *i.e.* it needs the application of Heat to bring it about.

Reactions in which Heat is evolved are called "*exothermic*" reactions, whilst those in which Heat disappears are called "*endothermic*" reactions, and compounds which are formed from their elements with the appearance or disappearance of Heat are called exothermic and endothermic compounds respectively.

The number of units of Heat (calories) evolved (or absorbed) during any chemical reaction is quite definite for definite weights of the reacting substances, and its amount has been determined in many cases.

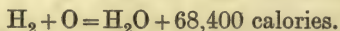
These determinations are made by causing the reaction to take place in such a way that all the heat produced is communicated to a known weight of water, and, from the rise (or fall) in the temperature of the water, the number of calories evolved (or absorbed) is readily ascertained.

For instance, when 2 grams of Hydrogen unite with 16 grams of Oxygen to form 18 grams of Water, 68,400 calories are evolved. This is an exothermic reaction.

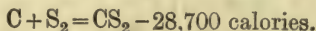
But, when 12 grams of Carbon unite with 64 grams of Sulphur to form 76 grams of Carbon Disulphide, 19,600 calories have to be supplied. This is an endothermic reaction.

The number of calories evolved or absorbed during a reaction is usually added on to the equation representing the reaction in the following way :

The first reaction quoted above is written

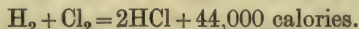


The second reaction, being endothermic, has the - sign, thus :

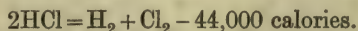


If the changes indicated in the reaction are reversible, then the heat evolved (or absorbed) is reversed also.

For instance, when Hydrogen combines with Chlorine the reaction is represented by the thermochemical equation :



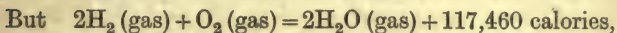
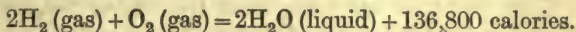
Therefore, if Hydrochloric acid has to be split up into Hydrogen and Chlorine, 44,000 calories will have to be supplied, and the equation is written :



In the first case there is a loss of Chemical Energy represented by 44,000 heat units, whilst in the second case there is a corresponding gain.

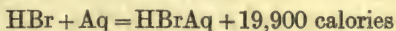
It must be very carefully noted that the state (solid, liquid

or gaseous) of the reacting bodies and the substances produced must be stated in the thermochemical equation, as the heat units evolved will naturally differ for different states. For example :



where, very clearly, the extra 19,340 calories are evolved by 36 grams of Steam condensing to Water.

When a *definite* quantity of Water takes part in a chemical reaction, such as the union of 18 grams of Water with 56 grams of Lime to form 74 grams of Calcium Hydrate, it is expressed in the equation by its formula H_2O , which represents 18 grams of Water, but, when a large mass of Water is involved, such as in the solution of a gas or solid in Water, it is customary to denote it by the symbol *Aq*, meaning a large quantity of Water. For example, the equation



indicates that when 81 grams of Hydrobromic acid gas dissolve in a large quantity of Water, 19,900 heat units are evolved.

Heat evolved (or absorbed) during the solution of gases or solids in Water is the resultant of two actions :

- (1) The loss of Chemical Energy.
- (2) The loss (or gain) of Latent Heat due to the change of state of the gas or solid.

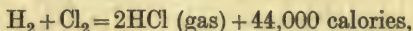
In the case of Hydrobromic acid gas, quoted above, the 19,900 calories are the result of the loss of Chemical Energy plus the Latent Heat evolved when gaseous Hydrobromic acid is condensed.

When a solid dissolves in Water the loss of Chemical Energy is opposed to the heat necessary to turn the solid into a liquid, and the result may be either a nett loss or gain, according as one is greater or less than the other. For instance, when Caustic Potash dissolves in Water, the loss of Chemical Energy is greater than the Heat Energy necessary to turn solid Caustic Potash into a liquid, and so the temperature rises, but when

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Ammonium Nitrate dissolves in Water, the opposite is the case, and so the temperature falls.

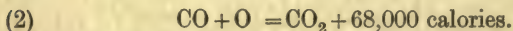
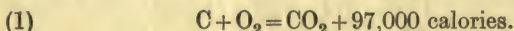
The number of heat units evolved when the weights (in grams) of the various elements represented in the formula of a compound unite is called the *Heat of Formation* of the compound. For instance, since



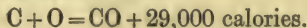
the Heat of Formation of Hydrochloric acid gas is 22,000 calories.

Comparatively few Heats of Formation are capable of being determined directly, but, by using these known data, it has been found possible to calculate the Heats of Formation of other compounds whose elements will not unite directly to form them.

For instance, Carbon and Oxygen will not unite directly to form Carbon Monoxide, but the Heat of Formation of this substance can be determined indirectly in the following way :

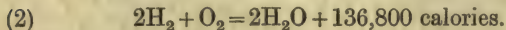
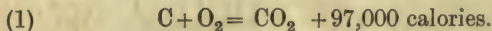


Both these reactions are capable of direct determination, and by subtracting (2) from (1),

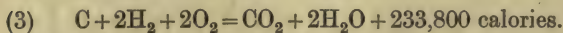


Hence the Heat of Formation of Carbon Monoxide is 29,000 calories.

Another example is seen in the manner in which the Heat of Formation of Marsh gas can be determined :



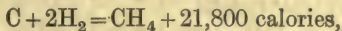
By addition,



When Marsh gas is burnt directly in Oxygen,



Hence, by subtracting (4) from (3),



and, in this way, the Heat of Formation of Marsh gas from Carbon and Hydrogen, two elements which will not unite directly to form Marsh gas, is ascertainable.

PROBLEMS.

41. The combustion of 46 grams of Ethyl Alcohol ($\text{C}_2\text{H}_6\text{O}$) liberates 340,530 calories. The Heats of Formation of Water and Carbon Dioxide are 68,360 and 96,960 calories respectively. What is the Heat Formation of Alcohol ?
(Camb. Univ. Schol. Exam.)

42. 12 grams of Carbon, when burnt in Oxygen, liberate 97,000 calories, but when burnt in Nitrous Oxide gas (N_2O) liberate 133,900 calories. Determine the Heat of Formation of Nitrous Oxide.
(Camb. Univ. Schol. Exam.)

CHAPTER XV.

ELECTROLYSIS AND THE IONIC HYPOTHESIS.

If an electric circuit is set up as in the diagram (Fig. 47), and various liquids and solutions are placed in the vessel *A*

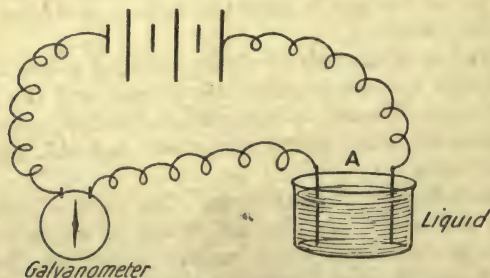


FIG. 47.—Determination of Conductivity of Liquids.

and tested as to their power of conducting an electric current, results somewhat as follows are obtained :

Liquid metals such as Mercury are *conductors*.

Pure Water and liquids like Turpentine, Benzene, Ether, etc., are *non-conductors*.

Certain classes of substances, viz. Acids, Bases and Salts, either in a fused state or in solution in Water, are *conductors*.

Solutions of other bodies, such as Sugar, Chlorine gas, Alcohol, etc., in Water, are *non-conductors*.

It would seem then that, with the exception of liquid metals, electrical conductivity in liquids is confined to solutions

ELECTROLYSIS AND IONIC HYPOTHESIS 163

of certain classes of bodies, viz. Acids, Bases and Salts, in a certain solvent, Water, or to the same classes of bodies in a fused condition.

To these solutions the name of *Electrolytes* is given.

Not only is the current conducted by these liquids, but they are, at the same time, split up into two parts by the current, one part appearing at the pole where the current enters the liquid—the anode—and the other part at the pole where the current leaves—the cathode.

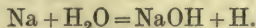
For instance, when a strong current is passed through molten Salt, the metal Sodium appears at the cathode and Chlorine gas is evolved at the anode.

Similarly with a solution of Copper Chloride, Copper is deposited upon the cathode and Chlorine is found in the solution round the anode, until the water is saturated with it, when it is evolved.

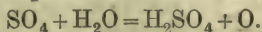
This process of splitting up a compound substance by means of an electric current is called *Electrolysis*, and the parts of the compound liberated at the poles are called *ions*, the one at the cathode being called the *cation*, and the one at the anode the *anion*.

Secondary Actions in Electrolysis. The result of electrolytic action is not always so straightforward as indicated in the examples quoted above, for secondary actions are frequently set up between the ions liberated and the solvent.

A typical instance of this is seen in the electrolysis of Sodium Sulphate. When a solution of this substance is electrolysed, Sodium is liberated at the cathode first, but it is attacked immediately by the water; Hydrogen gas is liberated and Caustic Soda formed, thus:



Simultaneously there is liberated at the anode the group SO_4 —called Sulphion—which, in its turn, attacks a molecule of Water forming Sulphuric acid and liberating Oxygen.



Thus, the gaseous products of this electrolysis are the same as those produced by the electrolysis of Water, whilst

the Salt is split up, round the poles at any rate, into the Base and Acid from which it is formed.

If the poles are kept apart by arranging the apparatus as in the diagram (Fig. 48), the Caustic Soda, which appears

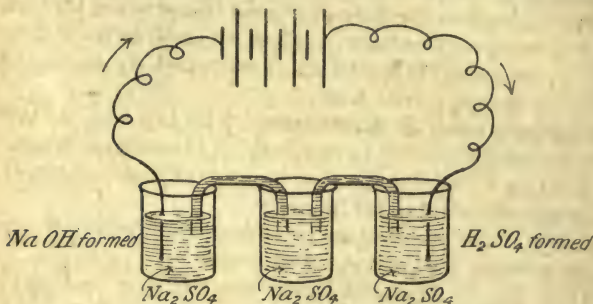


FIG. 48.—Electrolysis of Sodium Sulphate.

round the cathode, will turn red litmus blue, and the Sulphuric acid at the anode will turn blue litmus red, whilst neutral litmus placed in the central vessel will remain unchanged for a long time.

Electroplating. The deposition, during electrolysis of a metal from solution at the cathode, is made use of commercially for the process of electroplating, which process usually consists in the coating of some baser—*i.e.* more readily oxidizable—metal with a nobler metal which will resist oxidation.

In such a process as Nickelplating, where Steel is coated with Nickel to keep its surface bright and prevent the formation of rust, the Steel article to be plated is made the cathode in the electrolysis of a solution of Nickel Ammonium Sulphate, and Nickel is deposited upon it, (the Ammonia gas formed dissolves in the water); at the same time the Sulphur combines with some Nickel, of which metal the anode plates are made, forming Nickel Sulphate, so that the electrolyte retains its original strength.

Precisely similar processes are used for Silver and Gold plating, the electrolytes consisting usually of the Cyanides of the metals.

Electrolysis is also made use of to obtain perfectly pure specimens of metals, such as Copper. The impure Copper is made the anode in a bath of Copper Sulphate, and practically pure Copper, which contains 99.5 per cent. of the metal, is deposited on the cathode, the impurities dropping to the bottom of the tank in the form of mud.

The process has also been employed by swindlers for "sweating" sovereigns, a certain quantity, so small as to be detected only by weighing, being taken off each coin by making it the anode in an electrolytic bath.

Faraday's Laws of Electrolysis. Faraday was the first to investigate the quantitative results of electrolytic action, and he brought forward some very important facts concerning it. They are embodied in his Laws.

Law I. The weight of an ion liberated is directly proportional to the quantity of electricity which passes.

Thus, one Coulomb of electricity, which is unit quantity, deposits .001118 gram of Silver, and since one Ampère represents the passage of one Coulomb of electricity per second, a current of one Ampère will deposit .001118 gram of Silver per second. Two Ampères will then, by this Law, deposit .002236 gram of Silver per second, and so on.

It follows from this that, to deposit the Equivalent Weight of Silver in grams, i.e. 108 grams of Silver, the passage of 96,540 Coulombs of electricity is required.

This quantity is often called a Farad, after Faraday its discoverer.

Provided that there is no secondary action, the amount of electrical decomposition is not affected by the strength of the current, by the concentration of the solution, by the temperature or by the time during which the current is passed; the same quantity of electricity will always liberate the same weight of the ion.

Law II. When the same quantity of electricity is passed through different electrolytes, the quantities of the ions liberated are proportional to their chemical equivalents.

If the same current is made to pass simultaneously through electrolytic cells containing dilute Sulphuric acid, Silver

Nitrate, Copper Sulphate and Gold Chloride, the *weights* of the elements liberated after a certain time might be found to be somewhat as follows :

Electrolytes. Ions.	H ₂ SO ₄ .		AgNO ₃ .	CuSO ₄ .	AuCl ₃ .
	Cathode H.	Anode O.			
Weights liberated	·0133	·1063	1·4685	·422	·8738
If H = 1 - -	1	8	108	31·8	65·7
Atomic Weights -	1	16	108	63·5	197
Valency - -	1	2	1	2	3

These figures accurately prove the fact that the weights of the ions deposited are proportional to their chemical equivalents. Since these equivalent weights of the ions are liberated by the same quantity of electricity, it follows that this quantity either of positive or negative electricity must be carried by each monovalent ion, *e.g.* H or Ag, and be with it in all its movements through the electrolyte.

Similarly a bivalent atom, *e.g.* O or Cu, must carry double, and a trivalent atom, *e.g.* Au, treble the charge on a monovalent atom.

Accepting this view, it follows that the valency of an element is the number of these charges carried by its atom, and also that chemically equivalent quantities of matter have the same capacity for electricity.

Velocity of Electrolytic Conduction. By a series of experiments, Hopkins (1905) demonstrated the fact that an electric current passes through an electrolyte as quickly as through a wire of the same resistance, *i.e.* practically instantaneously, and it follows that the molecules of an electrolyte in solution must be in such a condition as to conduct the current immediately sufficient pressure (*i.e.* Voltage) is applied to overcome the resistance of the liquid.

The Ionic Hypothesis. These, and other considerations

have led to the putting forward of the Ionic Hypothesis, an hypothesis accepted nowadays by the great majority of chemists.

This hypothesis may be stated somewhat as follows. The molecules of every electrolyte in solution are constantly splitting up into two parts—the cation and the anion; these two parts carry equal (very large) charges of electricity, that on the cation being positive, and that on the anion negative in sign, and these ions are constantly reuniting together to form molecules which are, as constantly, splitting up again.

The cation is the metallic part of a Base or Salt, or Hydrogen in the case of an Acid, and the anion is the acid portion of an Acid or Salt, or Hydroxyl (OH) in the case of Alkalies.

For instance, in the case of a solution of common Salt (NaCl), the cation is Na, called Sodian to distinguish it from Sodium, and the anion is Cl, which is called Chloridion to distinguish it from Chlorine.

Similarly, in a solution of Sulphuric acid, there are two H ions, called Hydrions, each carrying a single + charge, and one SO_4 ion, called Sulphion, carrying a double – charge.

The properties of the ions are vastly different from those of the elements from which they are formed. In the ordinary way Sodium attacks Water at once, but Sodian does not. Chlorine has a yellow colour and a disagreeable smell, Chloridion is colourless and odourless; these differences in properties are explained by the large charges of electricity carried by the ions which evidently alter their properties very completely.

Notation. It is usual to express the fact that elements, or groups of elements, are in the ionic state, by appending to the symbols dots (·) in the case of cations, and strokes (') in the case of anions, the number of these depending on the valency of the ion.

Thus, H^{\cdot} represents mono-valent Hydrion, whilst $\text{Ca}^{\cdot\cdot}$ represents di-valent Calcion; similarly Cl' is the mono-valent Chloridion, OH' Hydroxydion of similar valency, whilst $\text{SO}_4^{\cdot\cdot}$ represents di-valent Sulphion.

Precipitation explained by the Ionic Hypothesis. The precipitation of difficultly soluble salts from solutions is very

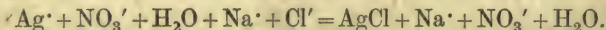
completely explained by the Ionic Hypothesis. For instance, it is a well-known fact that when solutions of Silver Nitrate and Sodium Chloride are mixed together, a white precipitate of Silver Chloride is thrown down and, if enough Sodium Chloride solution is added, the *whole* of the Silver disappears from the solution in the form of insoluble Silver Chloride.

The solutions before mixing contain :

- (1) Molecules of AgNO_3 , which are constantly dissociating into the cation Ag^+ and the anion NO_3^- .
- (2) Molecules of NaCl , which are also dissociating, forming the cation Na^+ and the anion Cl^- .
- (3) Molecules of H_2O , which only dissociate to a very limited extent into H^+ and OH^- .

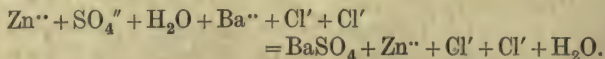
When free ions of Ag^+ and Cl^- meet in the solution, they form a molecule of AgCl , which, being insoluble in water, is precipitated and does not ionize again. In the course of a very short time, every Argention in the solution meets a Chloridion to combine with, and so the whole of the Silver disappears from the solution. At the same time, the Sodions and Nitrions are constantly uniting to form molecules of NaNO_3 , but these, being soluble in water, immediately split up again into their ions.

The reaction may be represented in the form of an equation, thus :



Thus, the Ionic Hypothesis very completely explains why the *whole quantity* of an element (or group of elements) disappears from a solution when an ion of the opposite kind, which forms with the element an insoluble salt, is introduced into the solution.

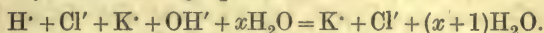
The complete precipitation of Sulphion SO_4^{--} from a solution by the addition of Barium Chloride, is shewn in the following equation :



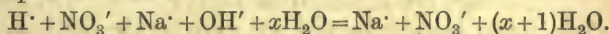
The amount of dissociation into ions which any soluble electrolyte undergoes depends on the strength of the solution

—the proof of this will be given later, p. 170. The more dilute the solution, the greater the number of ions compared with the number of molecules present in the solution, till, after a certain degree of dilution is attained, the whole of the solution is supposed to be in the ionic condition.

Heat of Neutralization. The neutralization of a dilute solution of Hydrochloric acid by a dilute solution of Caustic Potash—both solutions being completely ionized—is represented by the following equation :



Similarly, the neutralization of Nitric acid by Caustic Soda is represented thus :



If these equations are carefully examined, it will be noticed that the ultimate result, in both cases, is the union of Hydrion and Hydroxidion to form a molecule of Water, and a similar result would be arrived at for every case of neutralization of dilute acids by dilute alkalies.

It follows naturally from this that, if the Ionic Hypothesis is accepted, the heat evolved during the neutralization of equivalent weights of dilute acids and alkalies ought to be the same, whatever acid or alkali is used, being solely due to the combination of Hydrion and Hydroxidion.

To put this in a concrete form : when 50 c.c. of any $\frac{N}{100}$ Acid, are mixed with 50 c.c. of any $\frac{N}{100}$ Alkali, the heat evolved, if the Ionic Hypothesis is true, should be a certain definite number of calories.

Determinations of the Heat of Neutralization of a large number of equivalent weights of dilute Acids and Alkalies have been made, and a few of the results are appended :

Hydrochloric acid and Caustic Soda	evolve -	13,700 cal.
„ „ and Caustic Potash	„ -	13,700 cal.
„ „ and Calcium Hydrate	„ -	13,900 cal.
Hydrobromic acid and Caustic Soda	„ -	13,700 cal.
Nitric acid and Caustic Potash	„ -	13,800 cal.

These results are practically constant, and offer very strong confirmation of the truth of the Ionic Hypothesis.

Degree of Ionization. If experiments are made as to the electrical conductivity of solutions of electrolytes—Common Salt, for instance—it is found that, as the solution becomes more dilute, its conductivity becomes greater, but, after a certain stage of dilution is reached—and this is not till the solution is very dilute indeed—no further increase in the conductivity occurs.

This is explained by saying that the current is carried by the ions, and not by the molecules of the electrolyte, and consequently, the greater the degree of ionization, the better the conductivity, but that, when *all* the molecules become ionized, no further increase in conductivity can be attained however much the solution is diluted.

It is thus possible to determine roughly the degree of ionization of any electrolyte in a solution by comparing its conductivity with that of the same electrolyte in a solution of infinite dilution.

Thus, if a certain solution of Hydrochloric acid has a conductivity of 250, while an infinitely dilute solution has a conductivity of 350, the degree of ionization in the first solution is represented by the fraction $\frac{250}{350} = .714$. That is, 71.4 per cent. of the Hydrochloric acid molecules in the solution are supposed to be ionized, and the remaining 28.6 per cent. are in the form of molecules.

That solutions of different electrolytes of the same equivalent strength (*i.e.* the same fraction of the equivalent weight of each electrolyte dissolved in a litre of water) possess different electrical conductivities is well shewn by an experiment due to Whitney (1900).

The three tubes shown in the diagram (Fig. 49) contain solutions of Hydrochloric, Sulphuric and Acetic acids of strength such that one litre contains one-fifteenth of the Equivalent Weight of each acid. Electrodes are placed in both the upper and lower ends of each tube, the upper electrodes can slide up and down, but the lower ones are fixed.

The upper electrodes are connected, in parallel, with one terminal of an electric main supplying an alternating current of 100 volts, and the lower electrodes are connected, each through a glow lamp, to the other terminal of the same main. It is found that, when the terminals in each tube are an equal distance apart, the lamps connected with the three tubes glow with varying brightness, indicating differing resistances in the three circuits; that in the Hydrochloric acid circuit being the most brilliant, whilst that in the Acetic acid circuit scarcely glows at all.

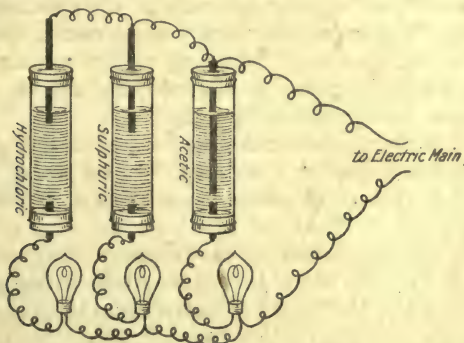


FIG. 49.—Conductivity of Electrolytes.

This indicates a different degree of ionization in the three acids, and, by adjusting the upper electrodes till the lamps all glow with equal brightness, the conductivities of the solutions will then be proportional to the distances the poles are apart. By measuring these distances a rough comparison of the degree of ionization in the three acids can be obtained.

In the solutions used above, the distances would be approximately as 100 : 85 : 1, which indicates that Hydrochloric acid molecules ionize more freely than those of Sulphuric acid, whilst the degree of ionization in Acetic acid molecules is very small indeed.

Strong and Weak Acids and Bases. The terms “strong” and “weak” were originally applied to acids according to

their power to turn one another out of their salts. For instance, Carbonic acid was accounted very "weak," because practically any other acid would turn it out of a Carbonate; similarly, Sulphuric acid was reckoned to be "stronger" than Nitric or Hydrochloric acids, because it would turn these acids out of Nitrates and Chlorides.

It is now recognized that the terms "less volatile" and "more volatile" are more applicable to this property of acids, as the question of which acid is to be turned out of a solution containing two acids is largely a question of their boiling points.

Latterly the terms "strong" and "weak" have been applied to Acids and Bases according to their electrical conductivity, *i.e.* to the degree of ionization they possess.

Consequently, according to this definition, both Hydrochloric and Nitric acids are "stronger" than Sulphuric acid, as their degree of ionization is greater, whilst Acetic acid is very "weak" indeed, as its degree of ionization is very small.

For the same reason Caustic Soda and Caustic Potash are "strong" bases, and the solution of Ammonia gas in water, which is usually called Ammonium Hydrate, NH_4OH , is a "weak" base.

The effect of Acids and Bases upon vegetable colouring matter, such as litmus, is due to the Hydrion (H') and Hydroxidion (OH') respectively, which are liberated in their solutions. Hydrion turns blue litmus red and Hydroxidion turns red litmus blue.

Consequently, the effects of salts upon litmus depend upon the respective strength and weakness of the Acids and Bases from which they are formed.

For example, Sodium Chloride formed from a strong acid, Hydrochloric acid, and a strong base, Caustic Soda, is neutral to litmus, as there is no tendency for either Hydrion or Hydroxidion to be liberated in its solution; on the other hand, Sodium Carbonate turns red litmus blue, being formed by the union of a strong base and a weak acid.

In a solution of Sodium Carbonate there are present ions of Sodium and of Carbanion CO_3'' , and also a certain small

number of Hydrions and Hydroxidions due to the partial ionization of the water. These latter are present in equal numbers, and so their effect upon litmus is neutral. But when, by the union of two Hydrions with Carbanion, a molecule of Carbonic acid, H_2CO_3 , is formed, this, being a weak acid, does not ionize again. Consequently, some Hydrions are taken out of the solution, leaving an excess of Hydroxidions, which turn red litmus blue. Of course, molecules of Caustic Soda NaOH are formed by the union of Sodions and Hydroxidions, but, being a strong base, they immediately split up again.

In a similar manner, a solution of Aluminium Chloride in water turns blue litmus red. Aluminium Hydrate, $\text{Al}(\text{HO})_3$, is a weak base. Hence Hydroxidions are taken out of the solution to form molecules, leaving excess of free Hydrions, which turn blue litmus red. A similar effect is seen in the case of Copper Sulphate solution. Sulphuric acid is a strong acid and Copper Hydrate a weak base, and so the solution of this salt is acid to litmus.

Another case is that of Potassium Cyanide, KCN , when dissolved in water. It ionizes first into K^+ and CN^- , the latter ion then unites with some free H^+ from the water, forming Hydrocyanic acid HCN , which is weak and remains as a molecule, so that the solution always smells of Hydrocyanic (Prussic) acid, and yet is alkaline owing to the presence of free Hydroxidions.

These three or four examples seem to be the reverse of neutralization, being the splitting up of a Salt into its Acid and Base. To this sort of process the term *Hydrolysis* is often applied.

PROBLEM.

43. One gram-molecule of Cane Sugar dissolved in 100 grams of Water lowered the Freezing Point by 18.90°C ., but one gram-molecule of Potassium Chloride dissolved in the same amount of water lowered the Freezing Point by 33.6°C . Calculate the degree of Ionization in the Potassium Chloride solution. (Camb. Univ. Schol. Exam.)

CHAPTER XVI.

LIQUEFACTION OF GASES.

THE relation between the volume of a gas and the pressure it exerts (or which is exerted upon it) is given by Boyle's Law, which states that, if the temperature is kept constant, the volume of a given mass of gas is inversely proportional to the pressure. Putting this a little more simply, if the pressure on a gas is doubled or trebled, the volume is halved or divided by three.

It is found, however, that no gas obeys this law when the pressure is sufficiently high, say 500 atmospheres, and that, for many gases, departure from the law begins at very low pressures.

This is because the gases are nearing the liquid condition, and several gases can be condensed to liquids, by increase of pressure alone.

The first gas to be liquefied in this way was Chlorine, and the experiment was performed by Northmore in 1806. Shortly afterwards Faraday succeeded in liquefying many gases, such as Chlorine, Sulphur Dioxide, Carbonic acid and Ammonia, by pressure only.

Faraday used always the simplest of apparatus, and his method consisted in causing the gas to be evolved in a confined space, so that the more gas which was formed, the greater the pressure, in fact he caused the gas to make its own pressure. For Chlorine, Faraday used a simple bent tube (Fig. 50), made of strong glass; the end was kept open, and into it he placed some crystals of Chlorine Hydrate, $\text{Cl}_2, 8\text{H}_2\text{O}$, passing

them along to the other end. He then sealed up the open end carefully and placed it in the position shown in the diagram.

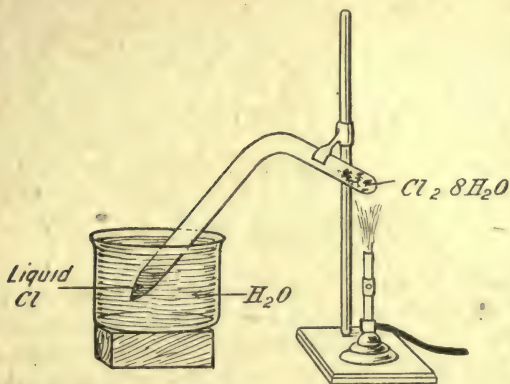


FIG. 50.—Liquefaction of Chlorine Gas.

The crystals were gently heated and evolved Chlorine steadily, the pressure increased, and finally yellow drops of liquid Chlorine condensed in the other limb, which was usually kept cool by being immersed in water.

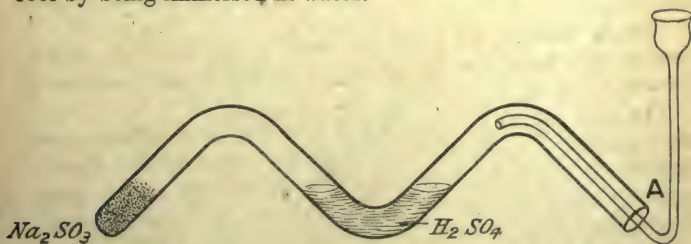


FIG. 51.—Liquefaction of Sulphur Dioxide by pressure.

For gases like Sulphur Dioxide or Carbon Dioxide, the gas was liberated by chemical means, instead of by heat, and a tube with a double bend in it (Fig. 51) was employed. Some solid Sodium Sulphite, Na_2SO_3 , or Sodium Carbonate,

Na_2CO_3 , was introduced into the closed end and strong Sulphuric acid was placed in the middle bend by means of a bent thistle funnel. The end *A* was then securely sealed up and the tube tilted till the acid came into contact with the solid at the closed end. Sulphur Dioxide or Carbon Dioxide was at once evolved, the pressure gradually increased, and finally liquefied gas was formed at the end *A* of the tube, which was immersed in cold water.

The following table gives, roughly, the pressures necessary to condense some of the more readily liquefiable gases at a temperature of $0^\circ \text{C}.$:

Gas.	Atmospheres.	Gas.	Atmospheres.
Sulphur Dioxide	1.5	Sulphuretted Hydrogen	10.0
Ammonia	4.5	Hydrochloric acid	26.2
Chlorine	9.0	Carbon Dioxide	38.5

Critical Temperature. Andrews shewed in 1869 that, if Carbon Dioxide is warmed above a certain temperature, no amount of pressure is sufficient to liquefy it. He determined this temperature very accurately (it was $31.35^\circ \text{C}.$), and called it the *critical temperature*.

All gases have a critical temperature, above which it is impossible to liquefy them by pressure alone, and these temperatures vary widely in degree. That of Sulphur Dioxide is $155.4^\circ \text{C}.$, of Chlorine $148^\circ \text{C}.$, whilst that of Hydrogen is as low as $-238^\circ \text{C}.$ This means that Hydrogen has to be cooled to a temperature 238 degrees below that at which water freezes before it can be liquefied, even by enormous pressures.

Some gases can be liquefied, at atmospheric pressures, by a lowering of temperature only; this is because the liquids formed have boiling points at temperatures which can be reached by freezing mixtures.

One of the easiest gases to liquefy in this way is Sulphur Dioxide, which has a boiling point of $-8^\circ \text{C}.$ To do this the carefully dried gas is passed through a worm tube (Fig. 52) surrounded by a freezing mixture of Ice and Salt. The gas condenses in the worm tube and runs down into the bottle prepared for it, which is also surrounded by a freezing mixture.

Some gases, such as Hydrogen, Oxygen, Nitrogen and Marsh gas, resisted for a long time all attempts to liquefy them, and to them the name of permanent gases was given, a name which they bore up to the year 1877. In that year, two famous experimenters, Pictet and Cailletet, by quite independent methods, succeeded in liquefying all these gases.



FIG. 52.—Liquefaction of Sulphur Dioxide by cooling.

Pictet's apparatus was of the same principle as Faraday's, but very complicated. His compression tubes were made of thick Copper, and in the case of Oxygen, the pressure was obtained by heating Potassium Chlorate in a strong wrought Iron retort. The Copper tube was kept at a very low temperature (the critical temperature is -119°C.), by surrounding it with a jacket containing liquid Carbon Dioxide, which was kept, by evaporation, at a temperature about -140°C. Pictet had most elaborate condensing and exhaust pumps for the work of liquefying the Carbon Dioxide and also the Sulphur Dioxide, which was used to liquefy the Carbon Dioxide.

Cailletet's method was much simpler. He did not attempt to get the gas below its critical temperature by intensely

cold freezing mixtures, but depended upon the fact that, if, when a gas is under very considerable pressure, this pressure is suddenly released, the quick expansion of the gas lowers its temperature to such an extent that it falls below the critical temperature and if the pressure, in spite of its reduction, is still great enough, the gas condenses.

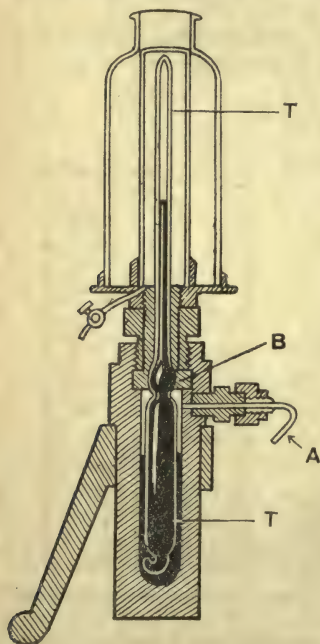


FIG. 53.—Cailletet's experimental tube.

The tube in which Cailletet conducted his experiments is shown in the diagram (Fig. 53). *TT* is a thick walled glass tube, made of a peculiar shape so as to fit exactly into the top of the pressure box at *B*. The lower part of the tube was of considerable dimensions, and the whole tube was first filled completely with the gas under examination, which was perfectly dry. The open lower end of the tube dipped under Mercury contained in the pressure box. This box was made sufficiently strong to withstand a pressure of 1000 atmospheres, roughly 7 tons to the square inch.

Water was next driven in to this box, above the Mercury, by means of a hydraulic pump, and the Mercury forced into the tube *TT* through the hole at the bottom. By this means the large volume of gas originally contained in the tube was compressed till it occupied only a very small portion of the thin part of the tube at the top. It was then cooled to some extent by surrounding the tube containing the compressed gas with cold water or a freezing mixture. The pressure was then suddenly

released by allowing the water to flow away, for a time, through a fairly large jet. The result of the sudden expansion of the gas thus produced caused a sufficient lowering of temperature to bring the gas below the critical temperature, and the tube became filled with a mist or fog consisting of very tiny particles of the liquefied gas.

A lowering of temperature, due to precisely similar causes, is produced when a gas at very high pressure is allowed to escape through a small orifice. This fact was first made use of by Dewar in 1894 for the liquefaction of the gases Oxygen and Nitrogen in air. At the same time, Linde and Hampson elaborated the idea, and Linde's apparatus is shown diagrammatically in Fig. 54.

In this apparatus air, at a pressure of 200 atmospheres, enters at *A* and passes through the inner of two concentric tubes, over 100 yards long, which are coiled in the form of a

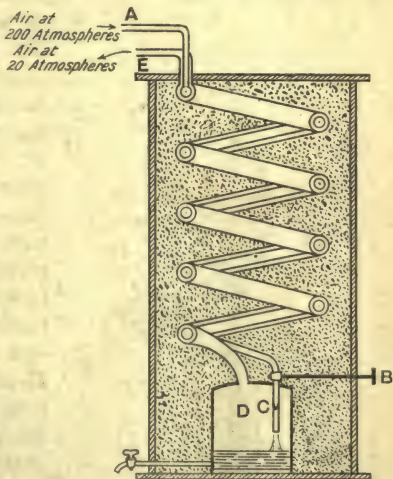


FIG. 54. —Linde's apparatus for liquefying air.

spiral and packed round with non-conducting material, such as wool or powdered cork, to prevent access of heat from the outside. At the lower end of this double-coiled tube is a valve *B*, connected with the inner tube, by the regulation of which the highly compressed air is allowed to expand suddenly through the jet *C* into the chamber *D*. By this expansion, the air is very much cooled, and this cold air passes through the outer of the coiled pipes, cooling the compressed air which is in the inner pipe. Eventually it escapes at the point *E*, having then a pressure of about

20 atmospheres, is returned to the compression pumps and enters the apparatus again at *A* at a pressure of 200 atmospheres much cooler than at first. In this manner, the air is gradually cooled more and more, till the critical temperature is reached, liquid air is formed, which falls into the chamber *D*, and is drawn off by a tap.

Liquid air has a temperature of about -190°C. , so that in an ordinary warm room it boils very rapidly. Dewar invented a receptacle for keeping it in the liquid form for quite a long time by preventing the access of external heat either by conduction or by radiation.

His *vacuum flasks* (Fig. 55) consisted of one round-bottomed flask inside a slightly larger flask, the two being hermetically

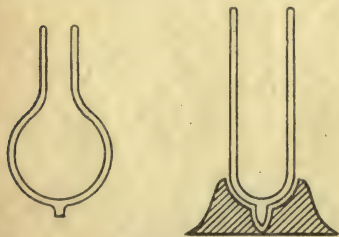


FIG. 55.—Dewar's vacuum flasks.

sealed together at the top. Through a small tube left on the bottom of the outer flask, the air was exhausted as perfectly as possible, and the small tube sealed up. By this means the annular space between the two flasks was quite vacuous, and, hence, no conduction could take place across it. To prevent radiation,

the outside of the inner flask and the inside of the outer flask were covered with a thin coating of Silver. In a flask like this 250 c.c. of liquid air will not all evaporate away in twenty-four hours.

This principle is now made use of, to a large extent, in the manufacture of the so-called "Thermos" flasks, which keep liquids either hot or cold for a long time.

By making use of the fact that liquid Nitrogen is more volatile than liquid Oxygen, Linde, by a modification of his apparatus, was able to separate the two constituents of air by fractional distillation and obtained Oxygen from air with only about 2 per cent. of Nitrogen as an impurity. This forms a very cheap and efficient method for the manufacture of Oxygen, and is largely employed at the present time.

The liquefaction of the more stable gases and their subsequent fractional distillation has been the source of several important chemical discoveries of late years. One of the most important was the discovery in air of the three very rare gases, Neon, Krypton and Xenon. Liquid Argon was subjected to very careful fractional distillation, and these gases were eventually isolated though present in almost infinitesimal quantities. Liquid Chlorine, Phosgene and other poisonous gases are made in large quantities, stored in cylinders, and let loose as 'poison gases' by the mere turning on of a tap. Similar liquids are also employed in shells, and slowly exude their noxious fumes when the shell strikes the earth.

Handwritten notes:
NaCl = HCl + NaOH
NaOH + HCl = NaCl + H₂O
HCl + NaOH = NaCl + H₂O
NaCl + H₂O = NaOH + HCl

CHAPTER XVII.

CHLORINE AND ITS COMPOUNDS.

CHLORINE.

Symbol, Cl. Atomic Weight, 35.45. Molecular Weight, 70.90.

Occurrence. Owing to the readiness with which this element combines with other elements, it is never found free in nature, but always in combination, usually with metals as their Chlorides.

By far the most common is Sodium Chloride, NaCl, or Common Salt, which is found in beds interdeposited with clays, and also dissolved in sea-water. An important deposit of the Chlorides of Potassium and Magnesium occurs as a bed at Stassfurt in Germany, and the Chloride of Silver is also found as a mineral deposit, and forms a very important ore of this metal.

Preparation. Whenever the Chloride of any metal is acted upon by Sulphuric acid, the Chlorine is liberated in combination with Hydrogen as Hydrochloric acid, from which compound-free Chlorine is more readily obtained than from the Chloride itself.

In order to effect the separation of Chlorine from Hydrogen in Hydrochloric acid, the Hydrogen is removed by causing it to combine with Oxygen, for which element it has, under certain conditions, a greater chemical affinity than it has for Chlorine.

In the laboratory this is brought about by causing a solution of Hydrochloric acid gas in water to act upon a Peroxide, the one most commonly used being Pyrolusite, Manganese

Dioxide, MnO_2 . The reaction between the two occurs on gently warming the mixture, and is represented by the equation

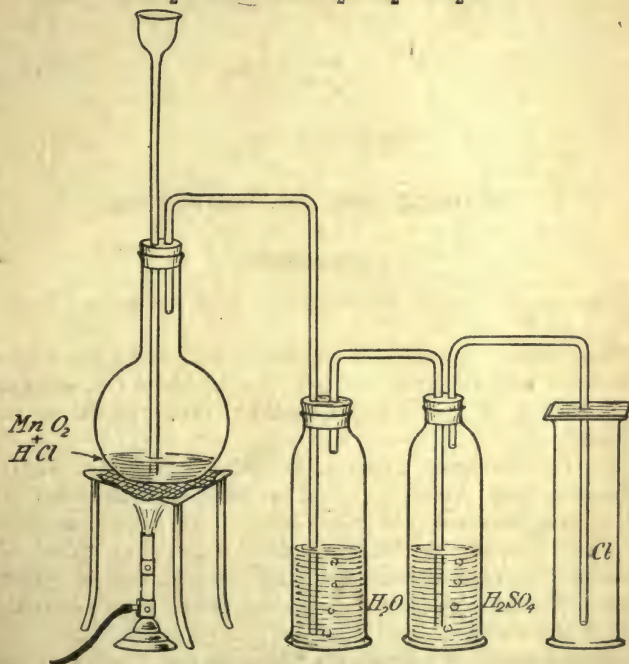
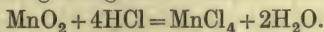


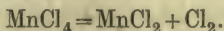
FIG. 56.—Preparation of Chlorine gas.

It is probable that this reaction occurs in two parts.

- (1) The Manganese Dioxide dissolves in the Hydrochloric acid forming Manganese Tetrachloride :



- (2) The Tetrachloride splits up, on gentle heating, into the Dichloride and Chlorine :



The experiment is conducted in an apparatus like that in the diagram (Fig. 56), the gas being first washed in order

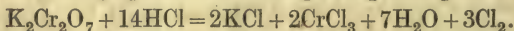
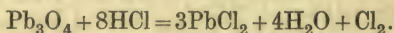
to get rid of any Hydrochloric acid gas or Manganese Dioxide, which may be carried over, then dried by being passed through strong Sulphuric acid, and finally collected in a *dry* gas jar by downward displacement.

Chlorine may be prepared directly from Common Salt, NaCl, by making a mixture of equal parts of Salt and Manganese Dioxide, and acting upon it with strong Sulphuric acid

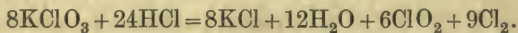


In this method Hydrochloric acid gas is liberated first from the Salt and Sulphuric acid, and this at once acts upon the Manganese Dioxide as shewn above.

Other oxidizing agents may be used instead of Manganese Dioxide to liberate Chlorine from Hydrochloric acid. The reactions with Red Lead and Potassium Bichromate are shewn in the following equations :

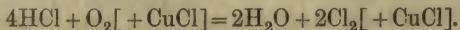


When a strong solution of Hydrochloric acid is caused to act upon Potassium Chlorate, a mixture of Chlorine and Chlorine Peroxide, ClO_2 , is evolved, thus :

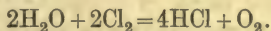


This mixture of Chlorine and its Peroxide was at one time thought to be a pure substance, and to it the name of *Euchlorine* was given. It forms a very powerful oxidizing agent, and is used as a medicine when dissolved in water.

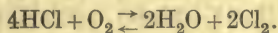
Deacon's Process. On a manufacturing scale, the Oxygen of the atmosphere is used to combine with the Hydrogen in Hydrochloric acid gas and liberate the Chlorine. This occurs when a mixture of Hydrochloric acid gas and air is passed through a tube containing pumice stone or broken bricks saturated with Cuprous Chloride (or Copper Sulphate) heated to a temperature of 400°C . The Copper salt acts as a Catalytic agent, as it is found to be unchanged in the tube at the end of the reaction.



Care must be taken that the pumice stone is not heated too strongly, as, above 600°C ., the reaction occurs in the opposite direction, thus :



This is, therefore, another example of a "reversible reaction," and the equation may be written thus :



Chlorine prepared in this way is necessarily contaminated with Hydrochloric acid, Steam and Nitrogen, but these impurities do not interfere with its use for the manufacture of Bleaching Powder, for which purpose the process is mainly used.

Electrolytic Methods. / Chlorine gas is evolved at the anode in several manufacturing processes in which fused Salt, or a solution of Salt, is electrolysed for making the metal Sodium or Caustic Soda or Washing Soda, and, since its escape into the air would be harmful as well as wasteful, it is usually converted into Bleaching Powder by allowing it to act upon slaked Lime.

Properties of Chlorine. Chlorine is a greenish-yellow coloured gas, with a disagreeable irritating smell. It attacks the membrane of the throat and nose, causing attacks of coughing and, if breathed in large quantities, it causes death.

Chlorine dissolves readily in cold water ; 100 volumes of water at 0°C . absorb 461 volumes of Chlorine, but at 20°C . only 22.6 volumes are dissolved. It is usually collected by downward displacement or over hot water as it attacks Mercury. Its aqueous solution when cooled below 0°C . deposits yellow crystals of Chlorine Octohydrate $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$. These crystals decompose at comparatively low temperatures, and are used for obtaining liquid Chlorine. The crystals are placed in one limb of a "Faraday tube" (Fig. 50), which is immersed in warm water. Chlorine is evolved and condenses, under pressure, as a yellow oily liquid in the other limb of the tube, which is kept very cold by immersion in a freezing mixture of ice and salt.

Action of Chlorine on other Elements. If Chlorine is thoroughly dry, it is a comparatively inactive substance, but the presence of a small quantity of moisture renders it most active. Moist Chlorine combines readily with nearly all the metals, forming their Chlorides. If inserted into jars of Chlorine when in a finely divided condition, metals such as Copper and Antimony take fire spontaneously. Other metals such as Iron, Sodium, Tin, etc., combine with Chlorine when heated in a stream of the gas.

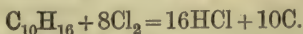
Yellow Phosphorus takes fire spontaneously in moist Chlorine, burning with a feebly luminous flame and forming poisonous fumes of Phosphorus Trichloride.

Its action with Hydrogen is particularly interesting. If equal volumes of Hydrogen and Chlorine are mixed in the dark, they do not appear to combine at all; in diffused daylight complete combination occurs in the course of a few hours, but, if the mixture is subjected to sunlight or to the light of burning Magnesium, the two gases combine instantaneously with an explosion. The volume of Hydrochloric acid gas produced is found to be exactly the sum of the volumes of Hydrogen and Chlorine before the union.

This great affinity which Chlorine has for Hydrogen is the cause of some of its most important reactions.

With Hydrocarbons—*i.e.* compounds containing Carbon and Hydrogen only—Chlorine reacts in two ways:

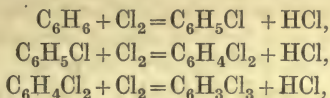
(1) With some, it combines with the Hydrogen, setting free the Carbon. Oil of Turpentine, $C_{10}H_{16}$, for instance, if introduced on a filter paper into a jar of Chlorine, takes fire spontaneously, forming white fumes of Hydrochloric acid and a black smoke of Carbon particles:



A burning taper, the wax of which is a Hydrocarbon, when introduced into a jar of Chlorine, goes on burning with a dull red flame, forming similar fumes to those formed with Turpentine.

(2) With other Hydrocarbons, such as Methane, CH_4 , or Benzene, C_6H_6 , Chlorine will replace the atoms of Hydrogen

one by one, forming Chlorides and liberating Hydrochloric acid :

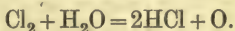


and so on till the final compound C_6Cl_6 is reached.

Such reactions are fairly common with organic substances, and the process is known as "*substitution*."

The bleaching action which Chlorine possesses is another result of its great affinity for Hydrogen. Dry Chlorine will not bleach a dry dye of any kind, but, if the Chlorine or the dyed substance is moist, then all vegetable dyes lose their colour when brought into contact with Chlorine, either in a gaseous state or in solution.

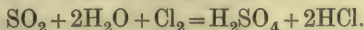
The reaction which occurs is probably that represented by the equation



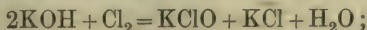
The Oxygen liberated, being "nascent" and in the atomic state, is much more powerful than ordinary molecular Oxygen O_2 ; it oxidizes the dyes and, the products of the oxidation being usually colourless substances, the dyes are bleached.

If a bottle of Chlorine water is left exposed to sunlight for a short time, or daylight for a considerable period, the reaction represented in the above equation occurs, Oxygen gas is liberated and a glowing splinter of wood may be rekindled by introducing it into the neck of the bottle. Owing to its action with water in this way, Chlorine is usually termed a strong oxidizing agent.

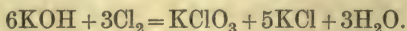
A good instance of its oxidizing power is seen in the reaction which takes place with Sulphur Dioxide in the presence of water, Sulphuric acid being formed thus :



With Caustic Potash, Chlorine reacts differently according to the conditions under which the action takes place. When it is led into a cold dilute solution of Caustic Potash, Potassium Hypochlorite and Potassium Chloride are formed, thus :



but, if the solution of Caustic Potash is concentrated and boiling, a mixture of Potassium Chlorate and Potassium Chloride results and, when the solution cools down, the Chlorate, on account of its lesser solubility, separates out in the form of crystals.

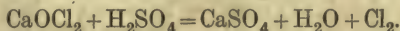


Bleaching Powder. When Chlorine gas is led into chambers containing Slaked Lime, Calcium Hydrate, $\text{Ca}(\text{OH})_2$, a large quantity of it is absorbed, forming a substance known as Chloride of Lime or Bleaching Powder. This substance is much used as a disinfectant and a bleacher.

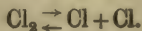
Its action, for both these purposes, is due to the readiness with which it parts with Chlorine; its disinfecting power being caused by the action of this gas as an oxidizer upon harmful substances, rendering them harmless.

The composition of Bleaching Powder has been the cause of much discussion; it may be considered to be a mixture of the Chloride and Hypochlorite of Calcium, $\text{CaCl}_2 + \text{Ca}(\text{OCl})_2$, and the formula usually given to it is CaOCl_2 , which is a combination of the two.

To use it for bleaching, the fabric is first dipped in a cold solution of the Bleaching Powder and then into a dilute acid, such as Hydrochloric acid or Sulphuric acid. The Chlorine is liberated and bleaches the dye.



The Molecular Weight of Chlorine. The density of Chlorine gas, below a temperature of 600°C ., is 35.45 ($\text{H}=1$); this indicates that the molecule of Chlorine contains two atoms, and is represented by the formula Cl_2 . Above 600°C ., the density decreases slowly, and at 1200°C . it is 23.6 *i.e.* about two-thirds of its normal value. This would seem to indicate that the molecules of Cl_2 are gradually dissociating into single atom molecules. This action is reversible, as the density increases again when the gas is cooled. It may therefore be represented by the equation



HYDROGEN CHLORIDE. HYDROCHLORIC ACID GAS.

Formula, HCl . Molecular Weight, 36.45.

History. The solution of this gas in water was known to the early alchemists; it was first prepared in large quantities by Glauber (1650), who obtained it by the action of Sulphuric acid on Salt. Priestley, who first examined its properties, called it "marine acid air," because of its preparation from Salt, and, for a similar reason, it is called Muriatic acid and also Spirits of Salt.

Preparation. As has already been noted, Hydrochloric acid gas is formed when Hydrogen and Chlorine are caused to

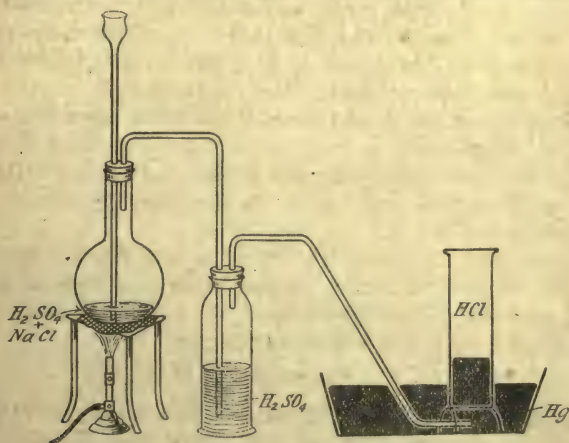


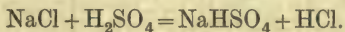
FIG. 57.—Preparation of pure Hydrochloric acid gas.

unite, either in diffused daylight or in sunlight, and, as nothing else is formed at the same time, this is conclusive evidence, by synthesis, of its composition.

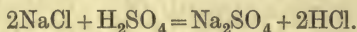
In the laboratory it may be prepared by the action of Sulphuric acid upon any Chloride; Sodium Chloride, being the cheapest, is the one most commonly used.

A mixture of Sulphuric acid and water in equal parts is poured on to some Salt crystals contained in a flask (Fig. 57),

and, on gentle warming, Hydrochloric acid gas is evolved. It is dried by passing it through strong Sulphuric acid, and, if wanted quite pure, it must be collected over Mercury, but if not, it may be collected by downward displacement. Under these conditions the reaction takes place according to the following equation, Sodium Hydrogen Sulphate being formed :



But, if strong Sulphuric acid is used, and a considerable amount of heat employed, further action takes place, and the normal Sodium Sulphate is produced :



Properties. Hydrochloric acid is a colourless gas with an acrid irritating smell. When allowed to escape into moist air, it dissolves in the water vapour, at the same time condensing it into small clouds (fumes) which consist of very tiny drops of the solution.

It is extremely soluble in water—1 c.c. of this solvent at 0°C . and 760 mm. dissolves more than 500 c.c. of the gas—with the evolution of a large quantity of heat ; for this reason the “ fumes ” of Hydrochloric acid gas are always warm.

It condenses fairly readily to a colourless liquid by the application of cold and pressure—at a temperature of -16°C . a pressure of 20 atmospheres is required—this liquid does not act on many metals which are vigorously attacked by the solution. Neither liquid Hydrochloric acid nor the *dry* gas has any action on blue litmus.

Hydrochloric Acid Solution. A solution of the gas in water is very much used in the laboratory. It is a very powerful solvent, many metals being dissolved in it, forming their Chlorides and evolving Hydrogen gas ; whilst a large number of chemical compounds, which are only very sparingly soluble in water, dissolve readily in the solution. It is used by plumbers for cleaning the “ dirt ” off metal surfaces before soldering them together.

The boiling points of solutions of Hydrochloric acid vary in a most interesting manner. The concentrated acid begins

to boil at low temperatures, giving off Hydrochloric acid gas, till a 20.24 per cent. solution is formed. This solution boils off unchanged at a temperature of 110° C. A weaker solution will begin to boil between 100° C. and 110° C., giving

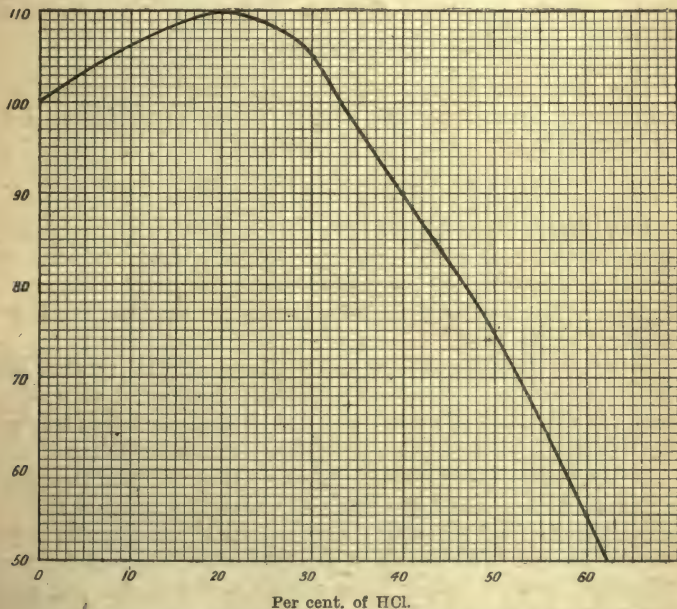


FIG. 58.—Boiling points of solutions of Hydrochloric acid gas under a pressure of 760 mm.

off steam till a 20.24 per cent. solution is left in the flask, which, as before, boils off unchanged. These facts are indicated in the accompanying curve (Fig. 58).

Composition of Hydrochloric Acid Gas. The composition of this gas, by synthesis, has already been indicated from its preparation by the combination of Hydrogen and Chlorine. By analysis, it may be shewn to contain Hydrogen, by passing the gas over Sodium metal contained in a bulb tube, when

a gas which possesses all the properties of Hydrogen is evolved and may be collected over water ; and the presence of Chlorine is shewn by substituting warmed Manganese Dioxide for the Sodium, in which case Chlorine gas is evolved and may be readily recognized.

If a closed tube, about 50 cm. long, is filled with pure dry Hydrochloric acid gas by passing the gas through it for a long time with a long delivery tube (Fig. 59), and then a few c.c. of Sodium Amalgam (made by rubbing small pieces of Sodium with a globule of Mercury in a mortar) are introduced into the tube and shaken up thoroughly with the gas, the open end of the tube being kept closed, meanwhile, by the thumb of the operator ; then, on placing this open end under water, and removing the thumb, the water is found to rise exactly half-way up the tube, and the residual gas, if tested, is found to be Hydrogen.

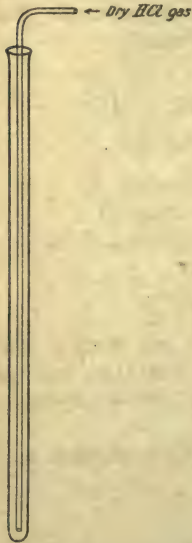


FIG. 59.—Composition of Hydrochloric acid gas.

This experiment proves that Hydrochloric acid gas contains half its volume of Hydrogen, but it must be carefully noted that it proves nothing at all about the quantity of Chlorine in the gas. Hence, by Avogadro's hypothesis, one molecule of Hydrochloric acid gas contains half a molecule, *i.e.* one atom of Hydrogen, and its formula may be written $\text{HCl}_{\frac{1}{2}}$.

When an aqueous solution of Hydrochloric acid is electrolysed, Hydrogen is evolved at the cathode, and Chlorine at the anode, which must therefore be made of Carbon, as Chlorine attacks Platinum. At first this Chlorine dissolves in the water, but, after the solution has become saturated with it, it is found that exactly equal volumes of Hydrogen and Chlorine are given off from the two poles.

Hence, if there is one atom of Hydrogen in the molecule of

Hydrochloric acid, there must be also one atom of Chlorine in it, and the formula is HCl.

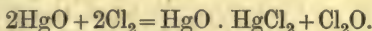
OXIDES OF CHLORINE.

Chlorine does not unite directly with Oxygen, but, by indirect methods, three Oxides of Chlorine have been prepared: Chlorine Monoxide, Cl_2O , Chlorine Peroxide, ClO_2 , and Chlorine Heptoxide, Cl_2O_7 . They are all very unstable compounds, and decompose with explosive violence.

CHLORINE MONOXIDE.

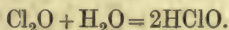
Formula, Cl_2O . Molecular Weight, 86.9.

Preparation. Chlorine Monoxide is obtained by passing dry Chlorine over dry Mercuric Oxide contained in a glass tube which is kept quite cool. The Oxy-Chloride of Mercury is left in the tube:



Properties. It is a pale yellow-coloured gas, with a smell very like that of Chlorine. It is most unstable, and decomposes violently into Chlorine and Oxygen with only a moderate rise of temperature.

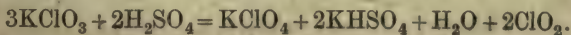
It dissolves readily in water forming Hypochlorous acid, HClO:



CHLORINE PEROXIDE.

Formula, ClO_2 . Molecular Weight, 67.45.

Preparation. Chlorine Peroxide is evolved by the action of Sulphuric acid on Potassium Chlorate. The finely powdered Chlorate is added, by degrees, to strong Sulphuric acid in a retort. A reddish liquid is formed, which, when warmed by being placed in a bath of warm water, evolves Chlorine Peroxide:



O.C.

N

As has already been seen, it is given off, mixed with Chlorine, when Potassium Chlorate is acted upon by Hydrochloric acid.

Properties. Chlorine Peroxide has a deep yellow colour and a most unpleasant smell; it produces headache if inhaled. It attacks Mercury and is fairly soluble in water, so it is collected by downward displacement as it is more than twice as heavy as air.

It is extremely unstable, decomposes gradually in daylight and with explosive violence when heated. Since Oxygen is set free by this decomposition, it is a powerful oxidizing agent.

If a mixture of Potassium Chlorate and powdered Sugar is made, and one drop of strong Sulphuric acid placed on it, the Chlorine Peroxide liberated causes combustion to start, and the whole mass inflames.

Yellow Phosphorus may be burnt under water in this gas by putting some crystals of Potassium Chlorate and one or two small pieces of Phosphorus at the bottom of a deep jar containing water; then, when a little strong Sulphuric acid is poured down the sides of the jar, the Chlorine Peroxide causes the Phosphorus to burn with bright flashes of light.

OXY-ACIDS OF CHLORINE.

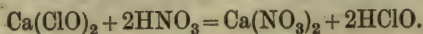
Three Oxy-acids of Chlorine are known: Hypochlorous acid, HClO , Chloric acid, HClO_3 and Perchloric acid, HClO_4 .

HYPOCHLOROUS ACID.

Formula, HClO . Molecular Weight, 52.45.

As has already been seen, Hypochlorous acid is formed when Chlorine Monoxide dissolves in water.

It may be prepared, in dilute solution, by distilling a mixture formed of a dilute filtered solution of Calcium Hypochlorite (Bleaching Powder) and very dilute Nitric acid:



Properties. Pure Hypochlorous acid has never been prepared, being an unstable compound, and it is only known in dilute solutions.

It is a strong oxidizing agent, owing to the readiness with which it parts with its Oxygen.

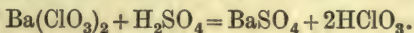
As an instance of this, if it is boiled for some time with a solution of Lead Acetate, a puce coloured precipitate of Lead Peroxide, PbO_2 is thrown down; similarly with Manganese Sulphate, Manganese Dioxide, MnO_2 is obtained.

The salts of this acid are called Hypochlorites, the best known is, of course, Calcium Hypochlorite or Bleaching Powder. These salts are all unstable bodies, and possess similar oxidizing properties to the acid itself.

CHLORIC ACID.

Formula, $HClO_3$. Molecular Weight, 84.45.

Preparation. This acid may be prepared, in dilute solution, by treating Barium Chlorate with an equivalent quantity of dilute Sulphuric acid:



↓

The precipitate of Barium Sulphate is allowed to settle, the clear liquid is poured off, and concentrated by evaporation in a vacuum (p. 109). By this means a 20 per cent. solution of the acid can be obtained.

Properties. A strong solution of Chloric acid possesses very powerful oxidizing properties; many organic substances such as paper or wood will take fire when the acid is dropped on them. and, even in dilute solutions, it is a powerful bleacher.

The salts of this acid are called Chlorates, and are much more stable than the acid itself. They are all soluble in water, and all yield Oxygen gas when heated. Potassium Chlorate, $KClO_3$, is the best known, and is of great value in the manufacture of fireworks.

PERCHLORIC ACID.

Formula, HClO_4 . Molecular Weight, 100.45.

Preparation. Perchloric acid may be prepared by distilling a mixture of Potassium Perchlorate and Sulphuric acid under reduced pressure :

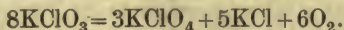


Properties. Perchloric acid is a colourless fuming liquid ; it produces serious wounds when it comes into contact with the skin. If dropped on to paper, wood or charcoal, these substances take fire with explosive violence.

It combines with water with a hissing sound, owing to the evolution of a large quantity of heat.

It is a mono-basic acid, and its salts are called Perchlorates. Potassium Perchlorate is the best known, and is one of the least soluble of the Perchlorates.

When Potassium Chlorate is gently heated till the first evolution of gas ceases, a mixture of Perchlorate and Chloride of Potash are left, and the two salts can be separated by fractional crystallization, owing to the much greater solubility of the Chloride. A possible equation for this reaction is

**PROBLEMS.**

44. Determine the volume of Chlorine gas evolved by the action of Hydrochloric acid on 5 grams of Pyrolusite containing 95 per cent. of Manganese Dioxide. The gas is measured at 14°C . and 745 mm. pressure.

45. A large lump of Zinc is placed in 100 grams of a solution of Hydrochloric acid. 125 c.c. of Hydrogen gas measured at 0°C . and 760 mm. are evolved. Calculate the percentage of Hydrochloric acid in the solution.

PRACTICAL EXERCISES.

To prepare the two Chlorides of Iron. Use a piece of glass tubing 20 cm. long and 1 cm. internal diameter. Place a loosely fitting plug of asbestos or glass wool in the centre of the tube, and put some Iron filings in one half. Fit the ends of the tube with corks, through each of which passes a short piece of glass tubing.

Heat the filings strongly in a bunsen flame, and, when red hot, pass *dry* Chlorine gas slowly over them. Ferric Chloride distils over and condenses in the form of brown crystals in the cool portion of the tube. When sufficient has distilled over, stop the flow of Chlorine and allow the tube to cool. Colourless crystals of Ferrous Chloride will condense on the Iron filings.

Both these substances are very deliquescent, but the crystals may be preserved by shaking them out of the tube into test tubes, which must be promptly corked up with rubber corks.

To show the Oxidizing action of Chlorine. Make a solution of Sulphurous acid (H_2SO_3) by bubbling Sulphur Dioxide gas through distilled water. Pass Chlorine gas for 5 minutes through this solution, and prove that Sulphuric acid (H_2SO_4) has been formed by adding a solution of Barium Chloride to the liquid, when a white precipitate of Barium Sulphate is thrown down.

To prepare some crystals of Potassic Chlorate. Make a strong solution of Caustic Potash in a beaker. Heat this solution till it is nearly boiling and pass Chlorine gas, which has been previously washed by water, through it for 10 minutes. Keep the solution hot all the time the Chlorine is passing through it. On cooling, crystals of Potassic Chlorate should separate out; if not, concentrate the liquid by boiling and cool it again.

Test the crystals by seeing if they evolve Oxygen gas when heated.

To find the strength of a Hydrochloric Acid Solution which has a Constant Boiling Point. Take about 30 c.c. of concentrated Hydrochloric acid in a beaker. Boil it, in a fume

cupboard, till its boiling point is constant at 110°C . Find the strength of the residual liquid by titrating 10 c.c. of it with N. KOH.

Place about 50 c.c. of dilute Hydrochloric acid in a retort and have a thermometer passing through the cork into the liquid. Boil it, and when the Boiling Point is constant at 110°C ., fit on a receiver and condense some of the distillate.

Find the strength of this distillate by titrating it with N. KOH.

Both these liquids should contain about 20 per cent. of Hydrochloric acid.

To prove that Hydrochloric Acid Gas contains half its Volume of Hydrogen. Perform the experiment described on page 192.

CHAPTER XVIII.

FLUORINE, BROMINE, IODINE AND THEIR COMPOUNDS.

FLUORINE.

Symbol, F. Atomic Weight, 19. Molecular Weight, 38.

Occurrence. Fluorine is found in nature in combination with various metals. The two best known minerals which contain it are *Fluor-Spar*, "Blue John," Calcium Fluoride, CaF_2 , which occurs most commonly in blue or green cubical crystals, and *Cryolite*, a double Fluoride of Sodium and Aluminium, Na_3AlF_6 .

Preparation. Though the presence of Fluorine in combination was recognized for a long time previous to 1886, it was not isolated till that date because of its active nature. M. Moissan was the first to prepare it, after an exhaustive series of experiments, by the electrolysis of a solution of Potassium Fluoride in Hydrofluoric acid. The addition of Potassium Fluoride was found necessary because pure Hydrofluoric acid does not conduct electricity.

This solution was placed in a U-tube made of an alloy of Platinum and Iridium, the poles being made of the same alloy, and Fluor-Spar stoppers were used. The whole U-tube was immersed in a bath of liquid Methyl Chloride, CH_3Cl , which boils at -23°C ., as, at higher temperatures, the Fluorine which is evolved at the anode attacks the Platinum-Iridium alloy. A diagrammatic form of the apparatus is shewn in Fig. 60.

Properties. Fluorine is a pale yellow-coloured gas which is extremely poisonous. It is the most active substance known. It combines with Hydrogen with an explosion, even in the dark and at very low temperatures. It decomposes Water with the formation of Hydrofluoric acid and the evolution of Oxygen, highly charged with Ozone.

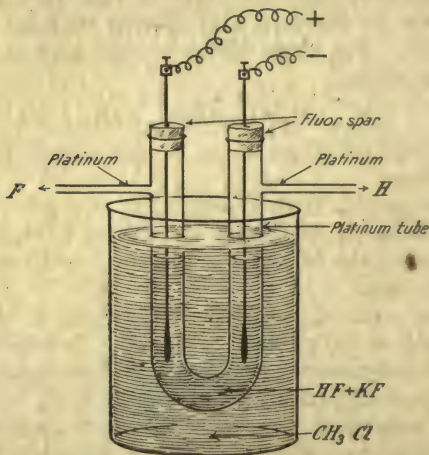


FIG. 60.—Preparation of Fluorine.

All the non-metals Sulphur, Bromine, Iodine, Phosphorus, Carbon, Silicon, Boron and Arsenic take fire when placed in the gas, forming their respective Fluorides.

All metals combine directly with Fluorine—some take fire spontaneously; others, such as Gold and Platinum, when heated to a temperature of $300^{\circ}C$.

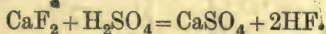
It forms no known compounds with Oxygen or Chlorine.

It liberates Chlorine from all metallic Chlorides, forming the Fluoride of the metal.

HYDROFLUORIC ACID. HYDROGEN FLUORIDE.

Formula, HF. Molecular Weight, 20.

Preparation. An aqueous solution of Hydrofluoric acid is obtained by distilling a mixture of Calcium Fluoride, CaF_2 , and concentrated Sulphuric acid in cast Iron retorts, and absorbing the Hydrofluoric acid evolved in Lead boxes containing water. The boxes themselves are kept cool by being immersed in water:



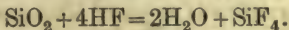
The acid solution is sent out in bottles made of Lead, Gutta-percha or Wax.

Pure anhydrous Hydrofluoric acid can be obtained by distilling Potassium Hydrogen Fluoride in a Platinum retort and condensing the fumes in a Platinum bottle immersed in a freezing mixture.

Properties. Anhydrous Hydrofluoric acid is a colourless fuming liquid at ordinary temperatures. It boils at 19.5°C . Both liquid and gaseous Hydrofluoric acid are deadly poisons.

It has a powerful affinity for water.

Its most interesting property is its action upon Silica, SiO_2 , and upon substances like Glass or Porcelain, which contain a large percentage of Silica. Either a solution of Hydrofluoric acid or the gas itself attacks Silica with the formation of Water and gaseous Silicon Fluoride, SiF_4 :



The solid matter of the Glass or Porcelain therefore disappears and, for this reason, a solution of Hydrofluoric acid is used for etching Glass.

In the process of etching, the object is first coated with a thin layer of Wax, which resists the action of the acid, and then the design to be etched is drawn on the Wax with a blunt tool exposing the Glass underneath. The Glass is then subjected to either gaseous Hydrofluoric acid for opaque etching, or to a solution of the gas for transparent etching, and, when

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finished, the Wax is washed off with Turpentine. The scales on glass instruments, such as thermometers or burettes, are marked in this way.

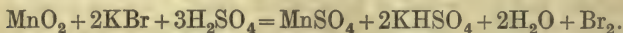
BROMINE.

Symbol, Br. Atomic Weight, 79.92. Molecular Weight, 159.84.

Occurrence. Bromine occurs in nature as the Bromides of Magnesium, Potassium, Sodium and Calcium. These salts are found in many mineral waters, in salt springs and in sea-water. The water of the Atlantic contains .007 per cent. of Magnesium Bromide, that of the Dead Sea .5 gram per litre of the same salt. Bromine is also found in many marine plants.

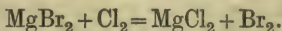
The main supply of Bromine, nowadays, comes from the salt beds of Stassfurt, which contain about 1 per cent. of Magnesium Bromide.

Preparation. In the laboratory, the simplest method of preparing Bromine is by acting upon a mixture of Potassium Bromide and Manganese Dioxide with Sulphuric acid. If the action takes place in a retort, the Bromine is evolved on gentle warming and the fumes may be condensed in a well-cooled receiver:



Compare this equation with the one used for preparing Chlorine by a similar method (p. 184).

Bromine is also obtained from any Bromide by displacing it with Chlorine. With Magnesium Bromide the action occurs as follows:



The solution becomes orange-yellow in colour owing to the separation of the Bromine, and if the liquid is heated the Bromine distils off and may be condensed. This method is the one adopted for the manufacture of Bromine from the "mother liquor" left after the salts of Potassium have been extracted from the Stassfurt deposits.

Properties. Bromine is a dark red heavy mobile liquid, which boils at 59°C . It is very volatile and gives off red vapours at ordinary temperatures. These vapours have a most disagreeable irritating smell—its name is derived from a Greek word meaning a stench—and they attack the eyes and mucous membranes of the throat and nose.

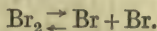
It is very poisonous and produces sores when dropped on the skin.

It is soluble in water; 100 grams of water dissolve 4.3 grams of Bromine at 0° ; it dissolves much more readily in Chloroform, Carbon Disulphide and Ether. If an aqueous solution of Bromine is shaken up with any of these liquids, the Bromine is taken from the water by the liquid, which separates out as a red layer—either below, or in the case of Ether, above, the water, and this layer contains all the Bromine present in solution. This reaction forms a very delicate test for the presence of free Bromine.

In its general properties Bromine resembles Chlorine in a less energetic form. It combines directly with most metals and non-metals. Its union with Hydrogen occurs slowly in sunlight, but more readily if the mixed gases are passed through a red-hot Silica tube. On account of its affinity for Hydrogen, it is a bleacher but of a very mild disposition.

Atomic and Molecular Weight of Bromine. By the analysis of Silver Bromide, the combining weight of Bromine is 79.92 when Silver is 107.88. As this is the smallest quantity of Bromine found in the molecule of any of its compounds, it is taken as the Atomic Weight of the element.

At 228°C ., the density of Bromine ($\text{H} = 1$) is approximately 79.5, which indicates the presence of two atoms in its molecule, but at 1500°C . its density is only about 53, shewing that the molecule is dissociating and becoming monatomic:



Uses. Bromine is used to a small extent in metallurgy, photography and other chemical industries. It is also used as a bleacher. The Bromides of Sodium and Potassium are used as medicines to induce sleep.

HYDROBROMIC ACID. HYDROGEN BROMIDE.

Formula, HBr . Molecular Weight, 80.92.

Preparation. Hydrobromic acid gas is formed by the direct union of Hydrogen and Bromine. If the mixed vapours are passed through a red-hot tube containing Platinized asbestos—asbestos covered with a thin deposit of Platinum—clouds of Hydrobromic acid gas issue from the end of the tube, the Platinum acting as a catalytic agent.

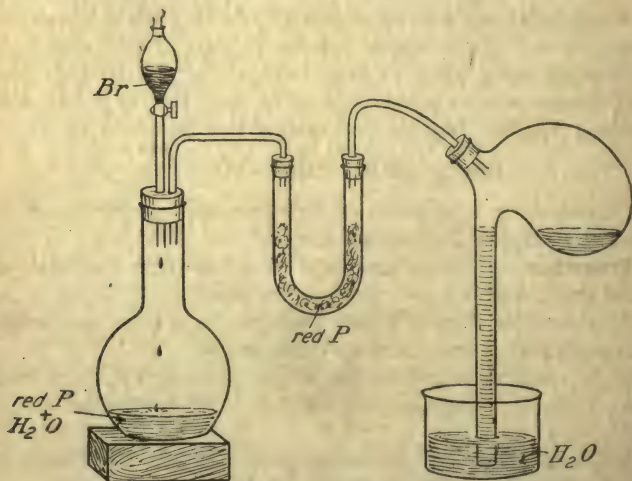
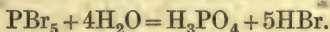
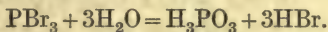


FIG. 61.—Preparation of a solution of Hydrobromic Acid.

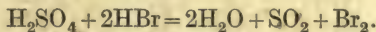
The best method of preparing a solution of the gas is by allowing Bromine to drop slowly from a dropping funnel (Fig. 61) into a flask containing a mixture of red Phosphorus and Water. As each drop of Bromine falls, a flash of light occurs, and volumes of Hydrobromic acid gas mixed with Bromine are evolved. The Bromine is absorbed by passing the mixed gases through a U-tube containing damp red Phosphorus and the Hydrobromic acid gas led into the top of an

inverted retort containing water. By this means the "sucking back" which would occur owing to the great solubility of Hydrobromic acid gas in water is prevented.

The chemical reactions which occur during this process are as follows. The Bromine first unites with the Phosphorus, forming Tri- or Penta-bromide of Phosphorus, and these substances react, at once, with the water thus :



When Sulphuric acid acts upon a Bromide such as Potassium Bromide, an action exactly similar to that of this acid upon a Chloride takes place at first, but part of the Hydrobromic acid formed acts as a reducing agent upon the Sulphuric acid, forming Sulphur Dioxide and setting free Bromine, thus :



Consequently a mixture of Bromine vapour, Hydrobromic acid and Sulphur Dioxide is evolved.

Properties. Hydrobromic acid is a colourless gas with an acrid smell, and it fumes strongly in the air.

It resembles Hydrochloric acid gas in all its properties, except that it is less energetic in its action.

It is even more soluble in water than Hydrochloric acid gas; 1 c.c. of water dissolves 600 c.c. of Hydrobromic acid at 0°C .

Its salts are called Bromides, and they are all soluble in water except the Bromides of Silver, Lead and Mercury.

OXY-ACIDS OF BROMINE.

No compounds of Bromine and Oxygen have been prepared as yet, but two oxy-acids are known.

They are called Hypobromous acid, HBrO , and Bromic acid, HBrO_3 . They resemble the corresponding Chlorine compounds in their methods of preparation and their properties.

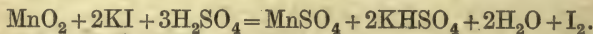
IODINE.

Symbol, I. Atomic Weight, 126.92. Molecular Weight, 253.84.

Occurrence. Iodine occurs in nature as the Iodides and Iodates of Magnesium, Potassium, Sodium and Calcium. It is found in many marine plants; those which live in deep water contain more Iodine than shallow-water seaweeds. It is largely extracted from the ashes formed when deep-sea weed is burnt; this ash is known as "kelp."

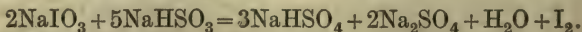
The Sodium Nitrate beds of Chili and Peru have recently been found to contain Iodine as Iodate of Soda, and the Iodine is obtained from the "mother liquor" left after the Sodium Nitrate has been extracted.

Preparation. In the laboratory Iodine is readily obtained by a similar reaction to that by which both Bromine and Chlorine are prepared. Sulphuric acid is added to a mixture of Potassium Iodide and Manganese Dioxide in a retort, the Iodine distils off on warming and may be condensed as black crystals:



Iodine is obtained from "kelp" by first getting rid of the less soluble salts contained in it—the Sulphates, Carbonates and Chlorides of Sodium and Potassium—by fractional crystallization, and then mixing the "mother liquor," which contains the Iodides of these metals, with Sulphuric acid and Manganese Dioxide and distilling off the Iodine.

The Chili Saltpetre—crude Sodium Nitrate—contains Iodine in the form of Sodium Iodate. When all the Nitrate has been crystallized out of a solution of the Saltpetre, the Iodate remains in the "mother liquor," and from it the Iodine is precipitated by acting upon it with Sodium Hydrogen Sulphite, thus:



Properties. Iodine is a black crystalline solid, which vaporizes slowly and has a smell resembling Chlorine. It

melts at 107°C. , and then gives off the violet-coloured vapour from which it derives its name.

It is only soluble in water to a small extent; 100 parts of water dissolve .32 parts of Iodine at 25°C. Its solubility in water is much increased when a crystal or two of Potassium Iodide are introduced into the liquid. The colour of this solution, as also that of its solution in Alcohol, is a deep brown, and both solutions are used in medicine as a tincture for external application.

Iodine dissolves quite readily in Chloroform, Carbon Disulphide and Ether, but these solutions are a violet colour.

When an aqueous solution of Iodine is shaken up with Chloroform or Carbon Disulphide, the Iodine is taken from the water by these liquids, which fall to the bottom as a violet-coloured layer.

Iodine resembles Chlorine and Bromine in its chemical properties, but is less energetic even than Bromine.

It combines with both metals and non-metals, forming Iodides, but only unites with Hydrogen with very great difficulty and in small quantities when the mixed gases are passed over red-hot platinized asbestos.

With a solution of Starch in water, Iodine forms an intense blue coloration. This reaction is so delicate that it will detect the presence of .0000001 gram of Iodine per c.c. of solution. The blue colour disappears on heating the liquid, but reappears on cooling. It is usually called Iodide of Starch, but its real composition is a matter of doubt.

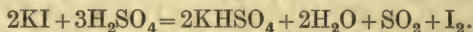
Atomic and Molecular Weights of Iodine. By the analysis of Silver Iodide, the combining weight of Iodine is found to be 126.92, and this is taken as its Atomic Weight, as no less quantity is found in the molecule of any of its compounds. The density of Iodine vapour at 600°C. is 126 ($\text{H}=1$), hence its molecule at that temperature is diatomic, but this value gradually decreases as the temperature rises, and, at 1500°C. , it is about 72. This indicates that the diatomic molecules of Iodine, like those of Bromine, dissociate into monatomic molecules at high temperatures.

HYDRIODIC ACID. HYDROGEN IODIDE.

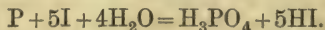
Formula, HI. Molecular Weight, 127.92.

Preparation. When a mixture of Iodine vapour and Hydrogen is passed through a tube containing red-hot Platinized asbestos, Hydriodic acid is formed, but only in small quantities.

It cannot be prepared pure by acting upon an Iodide with Sulphuric acid, as it reduces the Sulphuric acid in a similar manner to Hydrobromic acid, forming Sulphur Dioxide and Iodine. Thus, with Potassium Iodide :

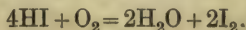


It is best prepared by allowing water to fall, drop by drop, into a flask containing a mixture of red Phosphorus and Iodine, and purifying the gas evolved from vapours of Iodine which pass over with it, by leading it through a U-tube containing red Phosphorus. The reaction is similar to that by which Hydrobromic acid is prepared :



Properties. Hydriodic acid is a colourless gas, which fumes strongly in air. It is very soluble in water—1 c.c. of water dissolving 425 c.c. of Hydriodic acid gas at 10° C.

This solution acts in a similar manner to those of Hydrochloric and Hydrobromic acids, and its salts are called Iodides. The solution is not very stable, and rapidly acquires a brown colour, owing to the precipitation of Iodine by oxidation, thus :

**OXIDES AND OXY-ACIDS OF IODINE.**

Iodine forms one compound with Oxygen, Iodine Pentoxide, I_2O_5 , and three oxy-acids, Hypoiodous acid, HIO, Iodic acid, HIO_3 and Periodic acid, HIO_4 .

These substances are comparatively unimportant.

THE HALOGEN GROUP OF ELEMENTS.

Fluorine, Chlorine, Bromine and Iodine form a group of elements with remarkable similarity in their properties and in their compounds. The name Halogen is applied to the group, because all four elements are found in sea-water.

The properties of the Halogens are graded in such a regular manner, that, if they are taken in the ascending order of their Atomic Weights—from Fluorine to Iodine—any property shews a regular increase or decrease in power. This is well shown in the following table :

Property.	F.	Cl.	Br.	I.
Atomic Weight	19.	35.45.	79.92.	126.92.
State - -	Gas.	Heavy gas.	Liquid.	Solid.
Melting point -	- 233° C.	- 102° C.	- 7° C.	+ 107° C.
Colour - -	Pale yellow.	Greenish yellow.	Red.	Violet.
Action with Hydrogen -	Unites in the dark at low temperatures with explosion.	Unites in sunlight with explosion.	Unites when the mixed gases pass through a red-hot tube.	Unites in small quantities when the mixed gases pass over red-hot platinized asbestos.
Solubility in water - -	Attacks water with violence.	Very soluble.	Less soluble.	Still less soluble.
Bleaching action - -	Destroys the fabric.	Excellent bleacher.	Poor bleacher.	Does not bleach.
Valency - -	All are mono-	valent in their	principal	compounds.

Groups of elements with similar properties are frequently met with in Chemistry. These groups form a convenient method of studying the various elements and their compounds, but the definite placing of all the elements in groups, though often attempted, is a difficult matter and, if adhered to too strictly, is apt to lead to wrong conclusions.

PROBLEMS.

46. 25 c.c. of a solution of Caustic Soda (strength 20 grams per litre) required 24.2 c.c. of a solution of Hydrobromic acid for exact neutralization. Calculate the strength of the latter.

47. 120 c.c. of Chlorine gas measured at 15° C. and 742 mm. are shaken up with a solution of Potassium Iodide. What weight of Iodine will be precipitated?

PRACTICAL EXERCISES.

To etch with Hydrofluoric Acid Gas. *N.B.*—This experiment must be done in a fume cupboard, as the gas is very poisonous. Cover the convex side of a watch glass with a thin coating of bees' wax or paraffin wax and remove part of the wax by scratching it with a blunt pin and exposing the glass underneath. Support the watch glass over a small leaden crucible, using wooden matches to prevent the watch glass coming into contact with the metal, and so melting the wax by conduction of heat. In the crucible place some Calcium Fluoride and strong Sulphuric acid and warm the mixture gently. Hydrofluoric acid gas is evolved and etches the glass where it is not protected by the wax. After ten minutes, take off the watch glass, warm it over a flame to melt away the wax, wipe with a cloth and the etching of the glass will be made plain.

To prove the presence of Bromine in a Bromide. Take a small crystal of any soluble Bromide in a test tube, dissolve in distilled water and add a few c.c. of Chlorine water. A yellow colour appears owing to the liberation of free Bromine; add 3 or 4 drops of Carbon Disulphide or Chloroform to the liquid and shake well. The Bromine is taken from the water by the Carbon Disulphide or Chloroform, which sinks to the bottom as a red coloured layer.

To prepare a Solution of Hydrobromic Acid. For this purpose use an apparatus similar to that described on page 204 (Fig. 61). Take about 5 grams of red Phosphorus and make it into a paste with Water. Use 2 or 3 c.c. of pure Bromine

in the dropping funnel and cover it over with a layer of Water to prevent the evolution of fumes. Test the Hydrobromic acid solution with litmus, with Magnesium powder and with a solution of Silver Nitrate.

To prepare the Iodides of Mercury. Take a small globule of Mercury in a mortar. Add to it, little by little, small crystals of Iodine, rubbing each crystal with a pestle till it combines with the Mercury. At first the green-coloured Mercurous Iodide is formed, but, as more Iodine is rubbed in, the colour changes to scarlet, and Mercuric Iodide is formed. Heat a little of this scarlet compound in a test tube. Note the change in colour; it is purely a physical change. There is no change in chemical composition.

N.B.—The combination between the Mercury and Iodine is accelerated by the presence of a few drops of Alcohol.

To prove the presence of Iodine in an Iodide. Dissolve a small crystal of any soluble Iodide in water and add to the solution a few c.c. of Chlorine water. The brown colour produced is due to the liberation of Iodine.

Shake up part of the brown liquid with 2 or 3 c.c. of Carbon Disulphide or Chloroform. The Iodine is dissolved out of the water and the heavy liquid sinks to the bottom, forming a violet-coloured layer.

Add one drop of the brown liquid to a solution of Starch made by putting boiling water on a little powdered Starch. Note the intense blue colour produced. Test the delicacy of this experiment by diluting the Iodine solution before adding it to the Starch.

To prepare a Solution of Hydriodic Acid. Use the same apparatus as for the preparation of Hydrobromic acid. Mix a few grams of Iodine and red Phosphorus in the flask and add water from the dropping funnel.

Test the solution obtained with litmus, with Magnesium powder and with a solution of Silver Nitrate.

Leave the solution exposed to the air for 24 hours and then test for free Iodine in it by means of Starch.

CHAPTER XIX.

SULPHUR AND ITS COMPOUNDS.

SULPHUR.

Symbol, S. Atomic Weight, 32.07. Vapour Density (at 500°), 95.3.

Occurrence. Sulphur, or as it is often called Brimstone (Burn-stone), occurs both in the free and combined states in nature. In the free state, native Sulphur is usually associated with either living or extinct volcanoes, and has doubtless been produced, in most cases, by the interaction of volcanic gases upon one another. The most important European sources are in Italy, Sicily and Iceland; deposits are also found in China, Japan, California and the Yellowstone district of the Rocky Mountains.

In combination, Hydrogen Sulphide is found in many mineral springs, and the Sulphides of many of the metals form very important ores, as, for example, *Cinnabar* or Mercury Sulphide, HgS , *Galena* or Lead Sulphide, PbS , *Blende* or Zinc Sulphide, ZnS , *Pyrites* or Iron Sulphide, FeS_2 , *Copper pyrites* or Copper Iron Sulphide, $(\text{CuFe})\text{S}_2$.

In combination with metals and Oxygen as Sulphates a few minerals are found, the best known being *Gypsum* or Calcium Sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, *Heavy Spar* or Barium Sulphate, BaSO_4 , and *Anglesite* or Lead Sulphate, PbSO_4 .

Extraction of Sulphur from its Ore. The Sulphur is separated from the greater part of the earthy matter with which it is associated by gently heating the ore, when, owing to its lower melting point, the Sulphur runs away from the rest

of the ore and is solidified separately. The product is known as "Crude Sulphur." The heat employed for this process is obtained by allowing part of the Sulphur to burn and thus supply heat for the melting of the remainder; about 25 per cent. of the Sulphur is lost in this way, but, as fuel is very costly in Italy and Sicily, this is a minor consideration.

The ore is stacked (Fig. 62) on a sloping floor, air spaces *A, A, A* being left at intervals for ventilation. The stack is covered over with burnt ore to exclude air as much as possible.

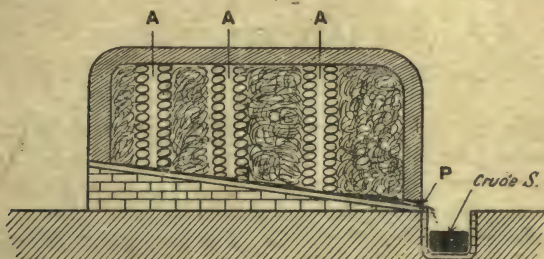


FIG. 62.—The preparation of Crude Sulphur.

The Sulphur is set alight at intervals round the sides and left for about five days to burn. The plug *P* is then removed and the crude Sulphur runs out into moulds.

The crude Sulphur is further purified by distillation. It is introduced into a large retort and boiled, the vapours passing over into a brickwork chamber. As the vapour enters, it is cooled and condenses upon the walls in minute crystals, forming a powdery deposit, which is scraped off and sold as "Flowers of Sulphur." If the distillation proceeds for some time, the walls of the brickwork chamber become hot enough to melt the Sulphur, which is run off from the bottom of the chamber into cylindrical wooden moulds, where it solidifies, forming "Roll Sulphur."

Properties of Sulphur. The element Sulphur exists in four distinct forms, whose physical properties differ very much, though chemically they contain nothing but the element.

These forms are spoken of as "allotropic modifications" of Sulphur, a term which will be discussed later.

Rhombic, Octahedral or α -Sulphur. This, the ordinary form of Sulphur, is a pale yellow brittle solid without taste or smell. It is a bad conductor of heat and electricity. If a piece of Roll Sulphur is held in the warm hand, it is heard to crackle owing to the breaking up of the outside layer by expansion during the warming, the heat not penetrating to any depth.



FIG. 63.—Rhombic or α -Sulphur.

Sulphur is insoluble in water, but dissolves quite readily in Carbon Disulphide, CS_2 , and by allowing a solution in this solvent to evaporate slowly, characteristic rhombic crystals (Fig. 63) are formed. Small crystals formed in this manner may be recognized under a microscope by their resemblance, in shape, to a "coffin."

Native crystals of Sulphur are always in the Rhombic form. Their specific gravity is 2.04.

Sulphur unites with Oxygen when heated in air or Oxygen, burning with a blue flame and giving off Sulphur Dioxide gas, SO_2 . If finely divided Sulphur is left in warm moist air, vaporization takes place, and hence it is often sprinkled on the hot water pipes of a greenhouse for purposes of fumigation.

Sulphur, especially in the form of vapour, unites with most metals, forming their Sulphides, often with the evolution of sufficient heat to produce incandescence. For example, if a coil of thick copper wire is placed in a test tube in which Sulphur is boiling, union takes place and the wire becomes red hot; on cooling it is found to have changed into grey Cuprous Sulphide, Cu_2S .

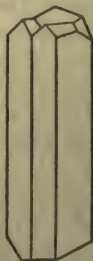


FIG. 64.—Monoclinic or β -Sulphur.

Monoclinic, Prismatic or β -Sulphur. If molten Sulphur is allowed to cool in a porcelain dish till a solid crust has formed on the surface and the still molten liquid is poured away from

under the crust by making a hole in it, long prismatic needle-shaped crystals are found on removing the crust.

These crystals belong to the monoclinic system and are shaped as in the diagram (Fig. 64). They differ in many respects from ordinary Sulphur. They are darker in colour, their specific gravity is 1.93 and their melting point is 120° C. instead of 115° C. Both varieties are soluble in Carbon Disulphide.

In about 24 hours, these needles become light yellow, opaque and brittle, and are found on microscopic examination to have changed into small rhombic crystals of α -Sulphur.

Plastic or γ -Sulphur. When boiling Sulphur is cooled suddenly by pouring it into cold water, it solidifies, forming a tough elastic material very like india-rubber. This variety is of a transparent amber colour. Its Specific Gravity is 1.95; it is insoluble in Carbon Disulphide.

On leaving it for an hour or two, it becomes hard, brittle and yellow in colour, reverting to the rhombic form. This change is accelerated by kneading it in the fingers or by chewing.

White, Amorphous or δ -Sulphur. When flowers of Sulphur are digested for some time with Carbon Disulphide, the Rhombic Sulphur is dissolved away, but it nearly always contains about 5 per cent. of insoluble Sulphur in the form of a white amorphous powder. This variety is stable at ordinary temperatures, but reverts to the Rhombic form when heated to 100° C.

The Effect of Heat on Sulphur. When some Roll Sulphur is very gradually heated in a test tube, it is found to melt at a temperature of 115° , forming a pale straw-coloured liquid. If this liquid is suddenly cooled by being poured into cold water, it solidifies into yellow Rhombic Sulphur. On heating the molten Sulphur above 120° C., it gradually darkens in colour, becoming red; it loses its mobility, and at temperatures between 160° C. and 180° C. is so viscous that the test tube may be held upside down without it falling out. Further heating causes its viscosity to diminish, and if now suddenly cooled plastic Sulphur is formed. Still further heating

darkens the colour still more till it is very nearly black, and at a temperature of 444° C. the liquid boils. The vapour at this point is of an orange-red colour, but at 500° C. it is deep red, and above 600° it is straw-coloured.

The Atomic and Molecular Weights of Sulphur. The combining weight of Sulphur was determined both by Dumas and Stas by passing Sulphur vapour over a weighed amount of heated Silver. By this method one gram of silver is found to combine with $\cdot 1485$ grams of sulphur, and if the combining weight of Silver is taken as $107\cdot 88$, that of Sulphur works out as $16\cdot 035$.

The least weight of Sulphur found in the molecule of any of its volatile compounds, such as Sulphuretted Hydrogen, H_2S , Sulphur Dioxide, SO_2 or Carbon Disulphide, CS_2 , is found to be $32\cdot 07$. This is taken as the Atomic Weight, and is twice the Combining or Equivalent Weight.

At a temperature of 500° C. the vapour density of Sulphur is about $95\cdot 3$ ($\text{H}=1$). This corresponds to a molecule containing 6 atoms, S_6 . On raising the temperature the vapour density gradually diminishes, till at 1000° C. it reaches $31\cdot 8$, corresponding with a molecule S_2 . Above this temperature further small diminution of density has been found to take place, indicating partial dissociation of the S_2 molecules into monatomic S molecules.

Allotropy. When an element exists, as Sulphur does, in several forms whose Physical properties are quite distinct, but, Chemically, they contain nothing but the element, it is called an Allotropic element, and the phenomenon is called Allotropy.

The proofs in the case of Sulphur may be set down as follows :

(1) Two of the varieties, namely, Monoclinic Sulphur and Plastic Sulphur, change gradually, *with no change in weight*, into Rhombic Sulphur.

(2) All four varieties when burnt yield the same readily recognizable gas, Sulphur Dioxide, SO_2 . This proves that they all contain Sulphur, but not that they contain nothing but Sulphur.

(3) When the same weight of each variety is completely burnt to Sulphur Dioxide and the gas absorbed and weighed, exactly the same weight of this gas is formed whichever variety is taken.

This experiment may be performed in the simple apparatus shewn in the diagram (Fig. 65). Pure dry Oxygen gas is passed slowly through a weighed bulb tube containing about half a gram of one of the forms of Sulphur; the latter is gently heated till it catches fire and then is allowed to burn very slowly. The Sulphur Dioxide gas formed is led through

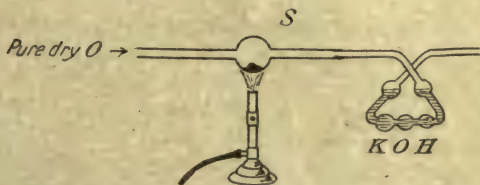


FIG. 65.—Synthesis of Sulphur Dioxide by weight.

Liebig's Potash bulbs—previously weighed—and if the combustion takes place very slowly, the whole of the gas is absorbed.

After a few minutes the flow of Oxygen is stopped and the apparatus allowed to cool, then, on reweighing, the loss of weight in the bulb tube gives the weight of Sulphur consumed, and the gain in weight of the Potash bulbs gives the weight of Sulphur Dioxide formed.

It is found that, for each variety, one gram of Sulphur produces very nearly two grams of Sulphur Dioxide.

This experiment also determines the equivalent of Sulphur with respect to Oxygen, for, since the equivalent of Oxygen is 8, that of Sulphur must be approximately 8 also; so that the equivalent with respect to Oxygen ($O=8$), is half that with respect to Hydrogen.

Other elements which have Allotropic varieties are Oxygen, which exists as Oxygen and Ozone, Carbon, Phosphorus and Silicon (*q.v.*).

The causes of Allotropy come probably under two heads :

(1) The different varieties possess different molecular weights, *i.e.* have different numbers of atoms in their molecules. This is undoubtedly the case as far as Oxygen and Ozone are concerned.

(2) The atoms which make up the molecule may be arranged or built up differently, just as two houses may be quite different in appearance, though built of the same kind of bricks.

HYDROGEN SULPHIDE. SULPHURETTED HYDROGEN.

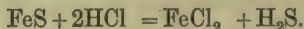
Formula, H_2S . Molecular Weight, 34.07.

Occurrence. Sulphuretted Hydrogen is found in the waters of many mineral springs, *e.g.* those at Harrogate in Yorkshire, in the gases which are evolved from volcanoes, etc. It is also formed by the putrefaction of both animal and vegetable bodies.

Preparation. When Hydrogen gas and Sulphur vapour are passed together through a red-hot tube, a certain amount of combination takes place, and Sulphuretted Hydrogen is formed. It is also produced in small quantity by passing Hydrogen through boiling Sulphur.

It is best prepared by the action of dilute Hydrochloric or Sulphuric acid upon Ferrous Sulphide, FeS .

The reactions which take place are shewn by the equations :



As this gas is always being required for testing purposes in the laboratory, an apparatus is required which will have the gas always "on tap," but will not generate it when it is not required. Many forms of apparatus have been designed for this purpose ; one of the most convenient is the one shewn in the diagram (Fig. 66.)

In this apparatus, when the tap *A* is opened, the acid comes into contact with the Iron Sulphide, but, as soon as the tap is closed, the gas generated drives the acid back again, and so

prevents further action. At *B* is a loosely fitting glass stopper, which prevents the solid Sulphide falling down into the acid below, but which allows the free passage of the acid in either direction.

Owing to the fact that Ferrous Sulphide is prepared by the action of Sulphur upon red-hot Iron, it usually contains free Iron as an impurity. This causes the Sulphuretted Hydrogen evolved to be contaminated with free Hydrogen.

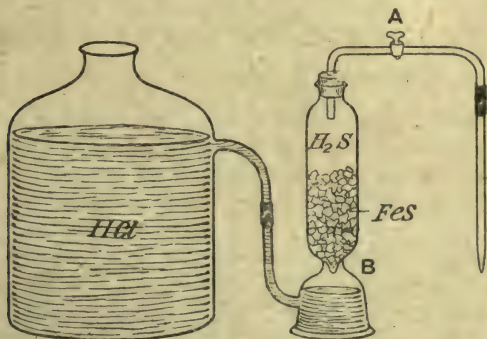
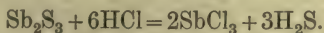


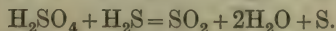
FIG. 66.—Apparatus for continuous supply of Sulphuretted Hydrogen.

Pure Sulphuretted Hydrogen is obtained by the action of boiling concentrated Hydrochloric acid upon the grey ore of Antimony, *Stibnite*, Sulphide of Antimony, Sb_2S_3 . The action is represented thus :



The gas evolved in the reaction, if washed in water to get rid of the Hydrochloric acid gas, is very fairly pure.

To dry the gas Calcium Chloride may be used, but Phosphorus Pentoxide is better ; Sulphuric acid must not be used, as it is reduced by the Sulphuretted Hydrogen, thus :



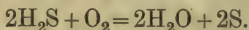
Properties. Hydrogen Sulphide is a colourless gas, with a very offensive smell resembling that of an addled egg.

It is a powerful poison when inhaled in the pure state; when diluted with air it produces headache. Lives have been lost by its inhalation by men cleaning out the chambers in which it has been absorbed during the purification of coal gas.

It is fairly soluble in water, 4.37 volumes of the gas being dissolved by 1 volume of water at 0° C. A dilute solution of the gas is used medicinally.

The solution in water reddens blue litmus; hence it is acidic, and is sometimes called Hydrosulphuric acid.

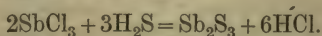
It may only be preserved in tightly-stoppered bottles which are kept in darkness, as it is readily oxidized by the Oxygen in the atmosphere, a yellow deposit of Sulphur being formed thus:



The aqueous solution or the gas itself is much used in the laboratory as a Reagent.

A *Reagent* may be defined as any substance which detects the presence of any other substance; thus Litmus is a reagent as it detects Acids and Alkalies, and Anhydrous Copper Sulphate is a reagent as it detects the presence of water. Hydrogen Sulphide is a reagent because it detects the presence of certain metals in solutions of their salts. The Sulphides of the metals are formed by double decomposition, and as many of these Sulphides are insoluble in water and acids, they are precipitated, and, as they also possess distinctive colours, they are readily recognized.

Thus, if Sulphuretted Hydrogen gas is bubbled through a solution of Antimony Chloride, an orange-coloured precipitate of Antimony Sulphide is formed:

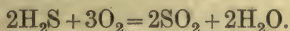


Similarly, solutions of Copper and Lead salts give dark brown or black precipitates of their respective Sulphides.

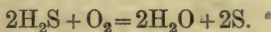
A few drops of Lead Acetate sprinkled on a piece of filter paper form a ready means of detecting Sulphuretted Hydrogen, as a very small quantity of the gas turns it black at once. The gradual discolouring of white paint in air is due to this gas.

as the basis of most paints is Carbonate of Lead, and this is changed to black Lead Sulphide by the Hydrogen Sulphide introduced into air by burning coal or coal gas.

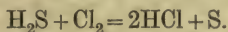
Sulphuretted Hydrogen is readily inflammable in air ; with plenty of air it burns with a blue flame, forming Sulphur Dioxide and Water vapour, thus :



If the supply of Oxygen is limited or if a jet of the burning gas is made to impinge on a cool surface, Sulphur is deposited thus :

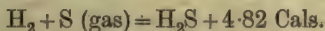


The halogens attack the gas, depositing Sulphur and forming the corresponding acid. Thus, in the case of Chlorine :



The gas also acts directly upon certain metals, forming their Sulphides ; Tin, Lead and Silver are at once attacked and become tarnished. The blackening of a Silver spoon by a partially decomposed egg is due to the formation of Silver Sulphide.

The union between the Hydrogen and the Sulphur in Hydrogen Sulphide is not a very strong one, very little heat being evolved when union takes place :

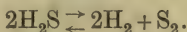


The gas is readily decomposed by passing it through a red-hot tube. Dissociation begins at 400° C. and is complete at about 1700° C.

If a series of electric sparks are passed through some Sulphuretted Hydrogen confined in an apparatus as in the diagram (Fig. 67), the gas is eventually completely decomposed, yellow Sulphur is deposited on the sides of the tube, and the residual gas, which has exactly the same volume as the original Sulphuretted Hydrogen, is found on testing to be pure Hydrogen.

It has been noticed (p. 218) that Hydrogen and Sulphur combine when the mixed vapours are passed through a red-hot

tube, so that this is an example of an opposing reaction, and the equation should be written



The reason why complete decomposition occurs under the action of the electric sparks is because the Sulphur is removed from the sphere of action by passing into the solid state.

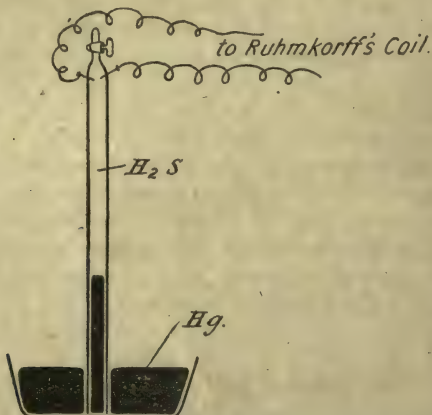
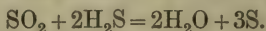


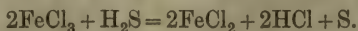
FIG. 67.—Decomposition of Sulphuretted Hydrogen by Electric Sparks.

Owing to the readiness with which it splits up into Sulphur and free (or nascent) Hydrogen, this gas is a strong Reducing Agent. Its action on Sulphuric acid has already been noted. When moist, Sulphur Dioxide gas is further reduced to Sulphur when mixed with Sulphuretted Hydrogen :



If strong Nitric acid is dropped into a jar of the gas, it is reduced with explosive violence.

When Hydrogen Sulphide is bubbled through a solution of Ferric Chloride, the latter substance is reduced to Ferrous Chloride, Sulphur being deposited :



Composition and Formula. It has been noticed that when a known volume of Sulphuretted Hydrogen is decomposed by a series of electric sparks, no change in volume takes place, and Hydrogen gas is left. A similar experiment may be performed by heating some Metallic Tin in the gas (p. 240).

These experiments shew that the gas contains its own volume of Hydrogen. Hence, by Avogadro's Law, since equal volumes of all gases at the same temperature and pressure contain an equal number of molecules, one molecule of Sulphuretted Hydrogen contains one molecule, *i.e.* two atoms of Hydrogen.

Hence the formula may be written H_2S_x , where x has yet to be determined.

Now the vapour density of Sulphuretted Hydrogen ($H=1$) has been found to be 17.13, hence its molecular weight is 34.26. When the weight of Hydrogen contained in the molecule, *viz.* 2, is deducted from this, the remainder is 32.26, which is very nearly the weight of one atom of Sulphur. Hence $x=1$, and the formula is written H_2S .

THE OXIDES AND OXY-ACIDS OF SULPHUR.

Sulphur has four known compounds with Oxygen, *viz.* :

Sulphur Sesquioxide or Hyposulphurous Anhydride	S_2O_3 .
Sulphur Dioxide or Sulphurous Anhydride	- - SO_2 .
Sulphur Trioxide or Sulphuric Anhydride	- - SO_3 .
Persulphuric Anhydride	- - - - S_2O_7 .

Of these, the first and last-named are comparatively unimportant, and only the Dioxide and Trioxide will be studied.

There are many oxy-acids of Sulphur; four are derived from the above-mentioned oxides, *viz.* :

Hyposulphurous acid	-	$H_2S_2O_4$.
Sulphurous acid	-	H_2SO_3 .
Sulphuric acid	-	H_2SO_4 .
Persulphuric acid	-	HSO_4 or $H_2S_2O_8$.

Derived from Sulphurous acid is a very important acid :

Thiosulphuric acid - - - $\text{H}_2\text{S}_2\text{O}_3$.

Besides these there is a series of acids called polythionic acids, viz. :

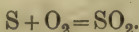
Dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$. Trithionic acid, $\text{H}_2\text{S}_3\text{O}_6$.
Tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$. Pentathionic acid, $\text{H}_2\text{S}_5\text{O}_6$.

SULPHUR DIOXIDE. SULPHUROUS ANHYDRIDE.

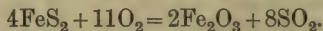
Formula, SO_2 . Molecular Weight, 64.07.

Occurrence. This gas is amongst those evolved from volcanic vents. It is also nearly always present in the air of towns, as it is formed by the combustion of the Sulphur compounds present in coal.

Preparation. Sulphur Dioxide is formed when Sulphur is burnt in air or in Oxygen :



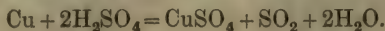
Some Sulphur Trioxide is also formed at the same time, the "fogginess" of the gas evolved being due to its presence. When Iron Pyrites or Copper Pyrites are "roasted," *i.e.* heated in a strong current of air, this gas is evolved :



This method is the one most commonly used for making the Sulphur Dioxide employed in the manufacture of Sulphuric acid.

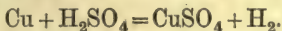
The usual laboratory method of preparation is by the action of hot concentrated Sulphuric acid on metallic Copper. Other metals such as Mercury, Silver or Zinc might be employed.

The usual equation given for this reaction is

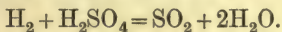


It is most probable that the action occurs in two stages :

(1) The acid attacks the metal, forming Copper Sulphate and nascent Hydrogen :



(2) The nascent Hydrogen reduces the Sulphuric acid with formation of Sulphur Dioxide and water :



The reasons for this statement are twofold : firstly, Sulphuretted Hydrogen gas is often evolved owing to the

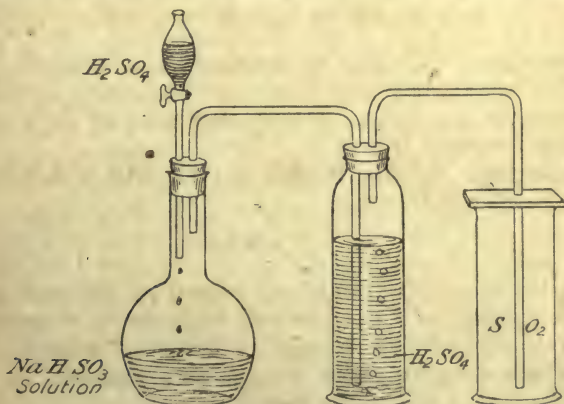
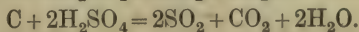
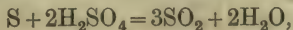


FIG. 63.—Preparation of Sulphur Dioxide gas.

further reduction of the Sulphuric acid ; secondly, the Copper turnings are, at the end of the reaction, found to be coated with black Cuprous Sulphide, Cu_2S produced by the reduction of the Copper Sulphate.

Sulphur Dioxide is also evolved when either Sulphur or Charcoal are boiled with strong Sulphuric acid, thus :



The latter reaction is employed in the manufacture of
o.c. P

Sulphites, as the Carbonic acid gas produced does not affect the reaction.

A convenient laboratory process for preparing the gas in small quantities is by placing a strong solution of Sodium Bisulphite, NaHSO_3 , in a flask and adding strong Sulphuric acid from a dropping funnel (Fig. 68) as required. The action is

$$\text{NaHSO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{H}_2\text{O} + \text{SO}_2.$$

The gas is dried by bubbling it through Sulphuric acid and collected by downward displacement.

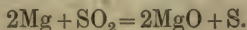
Properties. Sulphur Dioxide is a colourless gas with the strong suffocating smell associated with burning Sulphur. It is more than twice as heavy as air, its density being 2.2 (Air = 1). It is readily soluble in water, 1 c.c. of this solvent at 0°C . dissolving about 80 c.c. of the gas. The aqueous solution possesses strongly acid properties, and is generally called Sulphurous acid, H_2SO_3 ; hence the name Sulphurous Anhydride for the gas. On boiling, the acid disappears as such, and the whole of the Sulphur Dioxide is expelled.

By the action of pressure or cold, Sulphur Dioxide is readily condensed to a liquid. At 0°C . a pressure of 1.5 atmospheres causes it to condense, whilst at -10°C . it liquefies under ordinary atmospheric pressure.

Liquid Sulphur Dioxide can be readily made by passing the well-dried gas through a worm tube surrounded by a freezing mixture of ice and salt (p. 177).

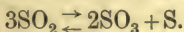
The liquid is made on a large scale and sold in thick glass "syphons," which are used as a ready means of obtaining supplies of Sulphur Dioxide in the laboratory or for the disinfection of sick rooms, etc.

If a piece of brightly burning Magnesium ribbon is introduced into a jar full of Sulphur Dioxide, it continues to burn with a spluttering noise; the gas is decomposed, Magnesium Oxide is formed and Sulphur deposited on the sides of the jar:



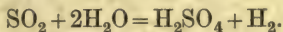
Sulphur Dioxide is decomposed by the influence of a strong light. If the beam of light from an arc lamp is passed through

a glass vessel containing the gas, it becomes cloudy after a time, owing to the formation of Sulphur Trioxide and free Sulphur, but, on removing the light, it recovers its transparency owing to the re-formation of Sulphur Dioxide :



Sulphur Dioxide is a powerful reducing agent. It decolorizes the red Permanganate of Potash, changes Chromates to salts of Chromium and Ferric salts into Ferrous salts.

Owing to its reducing action, it is a fairly strong "bleacher," and will take the colour out of rose leaves or magenta dye. It reacts with water, forming Sulphuric acid and nascent Hydrogen :

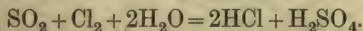


Its bleaching properties are due to the colourless substances formed with the nascent Hydrogen.

It is thus seen that its bleaching action is the exact opposite to that of Chlorine, which bleaches by oxidation.

Delicate fabrics and articles such as silk, sponges, flannel and straw are first bleached by Sulphur Dioxide because the use of Chlorine would destroy the fabric itself. Such substances gradually recover part of their original colour on continued exposure to air, owing to oxidation taking place and re-forming the original substance.

Sulphur Dioxide acts upon Chlorine in the presence of water, forming Hydrochloric and Sulphuric acids :



For this reason, it is employed as an "antichlor" in the operation of bleaching by Chlorine, to get rid of the last traces of Chlorine left in the fabric.

Composition. Its composition is determined by burning Sulphur in a known volume of Oxygen contained in an apparatus like that in the diagram (Fig. 69). When combustion

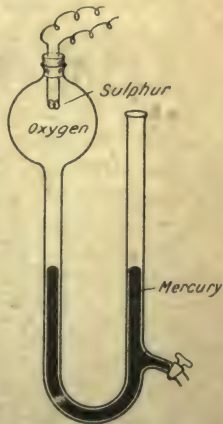


FIG. 69.—The composition of Sulphur Dioxide.

is completed and the Sulphur Dioxide cooled down to starting temperature, it is found to occupy precisely the same volume as the original Oxygen.

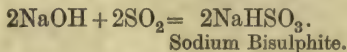
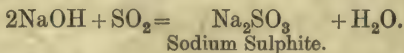
Hence, by Avogadro's Law, one molecule of Sulphur Dioxide contains one molecule of Oxygen, *i.e.* O_2 . The density of the gas ($H=1$) is found to be 32.03, and its molecular weight is consequently 64.06. Of this weight the Oxygen accounts for 32, so that the weight of Sulphur present in the molecule is 32.06, *i.e.* one atom of Sulphur.

This gives the formula SO_2 for the gas.

SULPHUROUS ACID AND THE SULPHITES.

The solution of Sulphur Dioxide gas in water is usually called Sulphurous acid, though the pure acid has not been prepared. It does not keep well, becoming oxidized to Sulphuric acid by the Oxygen of the air.

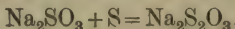
Sulphurous acid is a di-basic acid; it contains two atoms of replaceable Hydrogen and forms two series of Salts—called the Sulphites and the Bisulphites—when neutralized by a mono-valent alkali such as Sodium Hydrate, thus :



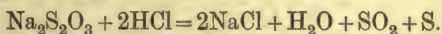
THIOSULPHURIC ACID AND THE THIOSULPHATES.

Preparation. When a solution of Sodium Sulphite, Na_2SO_3 , is exposed to air, it slowly takes up Oxygen, forming Sodium Sulphate, Na_2SO_4 . If the same solution is boiled with flowers of Sulphur an atom of Sulphur is taken up, forming the salt $Na_2S_2O_3$, which is called Sodium Thiosulphate (*i.e.* Sulpho-sulphate) because of the analogy between the two reactions.

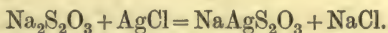
The Sodium salt is prepared in large quantities by the above-mentioned process, which may be represented thus :



Thiosulphuric acid itself has not been isolated; when the salts of this acid are acted upon by a mineral acid, *e.g.* Hydrochloric acid, the Thiosulphuric acid, which may be formed, immediately splits up into Water, Sulphur Dioxide and free Sulphur, thus:



Thiosulphuric acid has a great tendency to form double salts; for instance, when Sodium Thiosulphate is brought into contact with the Chloride, Bromide or Iodide of Silver, the double salt Sodium Silver Thiosulphate, NaAgS_2O_3 , is formed, thus:

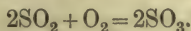


This double salt is soluble in water, hence the use of Sodium Thiosulphate, or, as it is wrongly called, Sodium Hyposulphite ("Hypo"), by photographers, for dissolving from photographic plates, films or papers, any excess of Silver salt which has not been acted upon by light.

SULPHUR TRIOXIDE. SULPHURIC ANHYDRIDE.

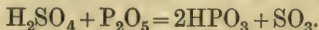
Formula, SO_3 . Molecular Weight, 80.07.

Preparation. When a well-dried mixture of Sulphur Dioxide and Oxygen is passed through a tube containing platinized asbestos, *i.e.* asbestos fibre covered with a thin deposit of metallic Platinum, the latter, when warmed to a temperature of 400°C ., acts as a catalytic agent, causing the union of the Sulphur Dioxide and Oxygen, and forming Sulphur Trioxide SO_3 :



The operation may be conducted in the apparatus shewn in the diagram (Fig. 70); the gases are dried by passing through strong Sulphuric Acid, and the Sulphur Trioxide formed is passed into a bulb, surrounded by a freezing mixture, where it condenses in the form of long white silky needles.

Sulphur Trioxide is also produced by the action of Phosphorus Pentoxide on strong Sulphuric acid ; when the mixture is gently warmed the Sulphur Trioxide distils off and may be condensed. Metaphosphoric acid remains behind :



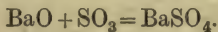
Properties. Sulphur Trioxide is a white crystalline silky-looking solid, which melts at 15°C . and boils at 46°C . Even at ordinary temperatures, the solid vaporizes without melting, and specimens kept in a closed tube will vaporize and condense again, apparently migrating from one part of the tube to another.



FIG. 70.—Preparation of Sulphur Trioxide.

It combines with water with great eagerness, forming Sulphuric acid ; great heat is evolved, so much so that part of the water is changed into steam, causing a hissing noise whenever the solid is brought into contact with water.

Sulphur Trioxide combines directly with many metallic Oxides forming their Sulphates ; with Barium Oxide, for example, so much heat is evolved that the mass becomes incandescent :

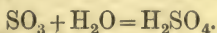


SULPHURIC ACID AND THE SULPHATES.

History. Sulphuric acid, perhaps the most important of all the acids, has been known for many years. Under the name of "*oil of vitriol*," a name which still sticks to it, its preparation from calcined Ferrous Sulphate and Sand was

described by Valentine in the fifteenth century. He also prepared it by burning Sulphur and Nitre together in moist air. This latter process was used on a comparatively large scale by Ward in 1740. The combustion was made to take place in a large glass bell-shaped vessel. His "oil of vitriol made by the bell" was famous, and sold for 2s. a pound, the old price being 2s. 6d. an ounce. Later a leaden chamber was substituted for the glass bell, and gradually the modern continuous process was evolved.

Preparation. As has already been seen, the solution of Sulphur Trioxide in water produces this acid :



Sulphur Trioxide is by no means easy to prepare ; on the other hand, Sulphur Dioxide can be readily and cheaply obtained in large quantities, but, even in solution, it oxidizes with great slowness, so that a means must be found to accelerate the oxidation.

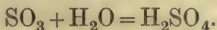
In the laboratory process, the necessary acceleration is produced by the higher oxides of Nitrogen, chiefly Nitrogen Peroxide, NO_2 .

A rough idea of the chemical actions is as follows :

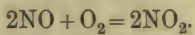
- (1) Nitrogen Peroxide and Sulphur Dioxide react, forming Sulphur Trioxide and Nitric Oxide :



- (2) With Water the Sulphur Trioxide forms Sulphuric acid :



- (3) Air (or Oxygen) is admitted and the Nitric Oxide combines with another atom of Oxygen, re-forming Nitrogen Peroxide :



This re-formation of Nitrogen Peroxide renders the action a "continuous" one, as it is ready to act upon more Sulphur Dioxide as in (1).

In actual practice, the apparatus shewn in the diagram (Fig. 71) is a suitable one. Into the large glass globe *A* is introduced, through the tube *a*, Sulphur Dioxide and Oxygen (or air), through *b*, Nitric oxide gas, through *c*, Steam, whilst *d* is an exit tube, and should be led into a fume cupboard. The Nitric Oxide and Sulphur Dioxide are introduced, first with an extra supply of Oxygen (or air), and then the steam is forced in. Dilute Sulphuric acid collects at the bottom of the glass globe.

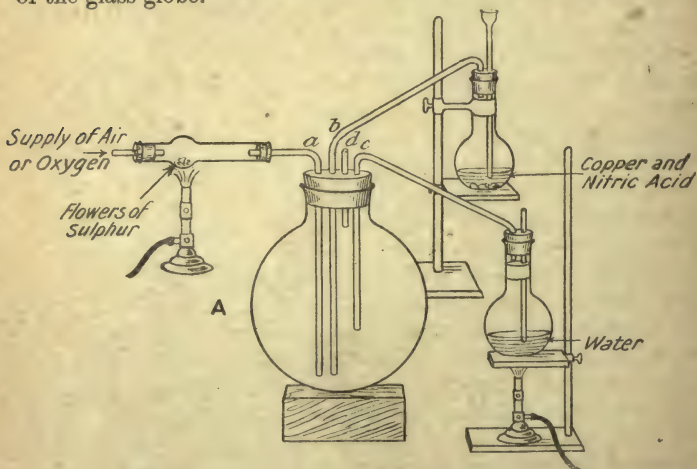
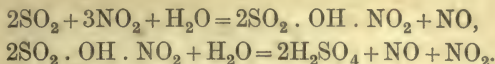


FIG. 71.—Laboratory preparation of Sulphuric Acid.

If only a small quantity of steam is allowed access to the globe, white crystals (known as "chamber crystals") are formed on its sides; these are an intermediate product formed during the reactions, and are called Nitro-Sulphuric acid. This compound may be regarded as Sulphuric acid $\text{SO}_2(\text{OH})_2$, in which one of the Hydroxyl (OH) groups has been replaced by the group NO_2 , and the formula $\text{SO}_2 \cdot \text{OH} \cdot \text{NO}_2$ is assigned to it. The chamber crystals at once dissolve and decompose when more Steam is admitted, forming Sulphuric acid, Nitric Oxide and Nitrogen Peroxide.

The equations shewing their formation and decomposition are given below :



This method of obtaining Sulphuric acid has been employed for many years on a manufacturing scale.

Sulphur or Iron Pyrites is burnt in a strong current of air to supply the Sulphur Dioxide and extra Oxygen, Nitric fumes are obtained by the action of Sulphuric acid on Saltpetre, and the mixture is made in large leaden chambers. To render the process economical, no Nitric fumes must be allowed to escape into the air. This is prevented by causing the gases which escape from the chamber to meet a stream of cold strong Sulphuric acid, trickling down a tower (the Gay-Lussac tower) filled with broken coke. The cold acid absorbs all the Nitric fumes, and is pumped up to the top of a similar tower (the Glover tower), up which pass the heated gases from the Sulphur or Pyrites burners. The hot gases deprive it of the dissolved Nitric fumes and pass them back into the chamber again.

Contact Process. In this more modern process Sulphur Trioxide is prepared by passing a mixture of Sulphur Dioxide and Air over platinized asbestos; the fumes are led up a tower packed with broken pieces of glass down which concentrated Sulphuric acid is trickling; the acid absorbs the fumes, forming a liquid with the approximate composition of $\text{H}_2\text{S}_2\text{O}_7$, *i.e.* $\text{H}_2\text{SO}_4 + \text{SO}_3$. This liquid is called "Oleum," and is used for "refreshing" dilute Sulphuric acid, bringing it up to concentrated strength.

In actual manufacture, the Sulphur Dioxide from the burners must be very carefully "cleaned" from dust, powdered

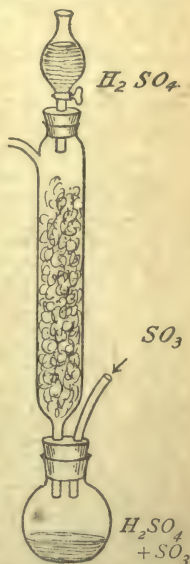


FIG. 72.—Preparation of Sulphuric Acid from Sulphur Trioxide.

Sulphur, Arsenic, etc., before allowing it to come in contact with the platinized asbestos, otherwise the latter quickly loses its efficiency as a catalytic agent.

The action proceeds most rapidly at a temperature of 400°C ., and since the heat of combination of the Sulphur Dioxide and Oxygen would tend to raise the temperature, arrangements are made by which it is kept very nearly constant at about 400°C .

Properties. Sulphuric acid is a colourless heavy oily liquid. It acquires a brownish tint after a time. This is due to its charring action on minute organic particles, dust, etc., which fall into it from the air.

Dilute Sulphuric acid gives off water when boiled, but an acid containing 2 per cent. of water distils over unchanged at a temperature of 338°C . If acid of this strength is cooled to 0°C ., it deposits pure Sulphuric acid in the form of colourless crystals, which melt at 10°C .

Sulphuric acid has a great affinity for water. It will absorb it from the air or from any gases which are made to pass over or bubble through the acid. On this account it is much used as a drying agent for gases, either by causing them to bubble through the acid or to pass over pumice stone which has previously been soaked in the concentrated acid.

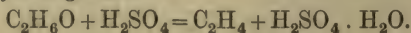
It has such a powerful affinity for water, that it will take it from many compounds which contain it.

Blue Copper Sulphate crystals are rendered white when placed in the acid owing to dehydration.

Carbohydrates, such as Cane Sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ and Starch or Cellulose, $\text{C}_6\text{H}_{10}\text{O}_5$ are charred by the acid, which abstracts the Hydrogen and Oxygen (being present in the same proportion as in Water), leaving black Carbon.

Sulphuric acid raises blisters when it comes into contact with the skin for a short time, owing to the abstraction of moisture, and, if kept in contact with human flesh for any length of time, it produces serious wounds.

From Alcohol, $\text{C}_2\text{H}_6\text{O}$, it abstracts the elements of Water, leaving Ethylene gas, thus:

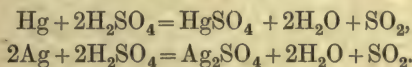


The mixture of Sulphuric acid and water gives rise to the evolution of a large quantity of heat. For this reason, in diluting the acid, water should never be added to the strong acid, always acid to water and that slowly, or dangerous explosions are apt to occur owing to the sudden formation of steam by the great heat given out. At the same time, after cooling a mixture of the acid and water, it is seen to have contracted in volume.

These two facts, the evolution of heat and contraction in volume, both point to the formation of definite chemical compounds. Two of these are actually known to exist, namely, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$.

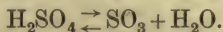
The action of Sulphuric acid upon metals is interesting. The cold concentrated acid has very little action on any metal, but if hot, it attacks all the more common metals with the exception of Gold and Platinum, forming the Sulphates of the metals and giving off Sulphur Dioxide gas.

This action with Mercury and Silver is shewn in the equations:



The dilute acid reacts with the metals Sodium, Potassium, Magnesium, Zinc, Iron, Cobalt, Cadmium and Manganese, forming the Sulphate of the metal and evolving Hydrogen.

The vapour of Sulphuric acid, when heated to 450°C . dissociates completely into Sulphur Trioxide and steam:

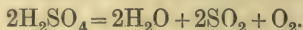


This is proved by the fact that its vapour density at 500°C . is only about one half of that required for the molecule of H_2SO_4 , shewing that the one molecule has dissociated into two, viz. SO_3 and H_2O .

At higher temperatures, still further decomposition takes place, the Sulphur Trioxide splitting up into Sulphur Dioxide and Oxygen.

This may be shewn by allowing the concentrated acid to fall, drop by drop, into a red-hot Platinum flask *A* (Fig. 73), condensing the acid vapours in the flask *B* and collecting

the Oxygen over water in *C*, most of the Sulphur Dioxide dissolving in the water :



Constitution. Sulphuric acid is a di-basic acid, since both the Hydrogen atoms contained in its molecule are replaceable by a metal. Consequently, with mono-valent metals, such as Sodium and Potassium, two series of salts are formed, containing one or two atoms of the metal per molecule of

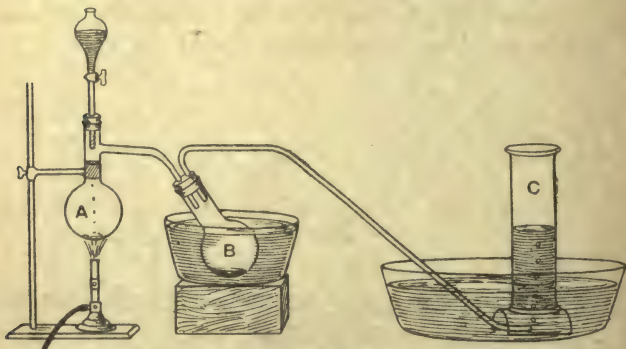


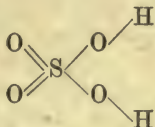
FIG. 73.—Decomposition of Sulphuric Acid by heat.

salt respectively. Where both atoms of Hydrogen are replaced, as in Na_2SO_4 , the salts are called normal Sulphates and are neutral to litmus, but where only one atom of Hydrogen is replaced, as in NaHSO_4 , the salts are called bi-sulphates or Hydrogen Sulphates.

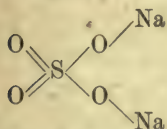
Salts of this type, which still contain unreplaced Hydrogen, are often called Acid salts because some of them turn blue litmus red, but the name is misleading, as many Hydrogen salts, *e.g.* Sodium Bicarbonate, NaHCO_3 , and Sodium Hydrogen Phosphate, Na_2HPO_4 , are respectively alkaline and neutral in their action towards litmus

The molecule of Sulphuric acid may be shewn by means of reactions, which belong rightly to the province of Organic chemistry, to contain two Hydroxyl (OH) groups, and its formula may be written $\text{SO}_2(\text{OH})_2$ to indicate this fact.

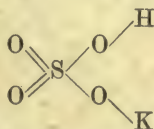
Structurally, since in compounds like Sulphur Trioxide, SO_3 and Sulphur Hexafluoride, SF_6 , an atom of Sulphur appears to be hexa-valent, the formula of Sulphuric acid may be written thus :



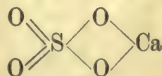
and it follows that the formula of some of its sulphates may be written, structurally, as indicated below :



Normal Sulphate
of Soda.



Bisulphate of
Potash.

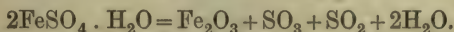


Calcium Sulphate.

PYROSULPHURIC ACID. NORDHAUSEN OR FUMING SULPHURIC ACID ($\text{H}_2\text{S}_2\text{O}_7$).

Preparation. Strong Sulphuric acid will still continue to dissolve Sulphur Trioxide. On cooling such a solution, Persulphuric acid separates out in the form of large colourless crystals.

Originally this "fuming oil of vitriol" was manufactured by heating the green crystalline Ferrous Sulphate (or green vitriol as it was and is still called), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, in clay retorts and condensing the distillate in receivers containing water; in the process, six molecules of the contained water of crystallization are driven off leaving the substance $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. Further heating decomposes this compound, leaving Ferric Oxide and driving off Sulphur Trioxide, Sulphur Dioxide and Steam :



Properties. Pyrosulphuric acid is a strongly fuming, colourless liquid which acts in most cases like Sulphuric acid. It

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forms, however, a series of salts called the Disulphates, of which Sodium Disulphate, $\text{Na}_2\text{S}_2\text{O}_7$, is a typical example. These salts are analogous to the Dichromates.

PROBLEMS.

48. What volume of Sulphuretted Hydrogen gas is evolved when 3 grams of Ferrous Sulphide are treated with Hydrochloric acid : (1) At standard temperature and pressure, (2) at 15°C . and 745 mm.?

49. 25 c.c. of Sulphuretted Hydrogen gas, measured at 10°C . and 740 mm., are led into a solution of Lead Nitrate. Determine the weight of the precipitate which is thrown down.

50. Find the weight of 150 c.c. of Sulphur Dioxide gas measured at 15°C . and 775 mm. pressure.

51. 25 c.c. of a solution of Iodine required 18.6 c.c. of a solution of Sodium Thiosulphate (strength 1.58 grams $\text{Na}_2\text{S}_2\text{O}_3$ per litre) for complete neutralization. Determine the strength of the Iodine solution in grams per litre. (For equation, see page 241.)

52. Excess of Potassium Iodide was added to 50 c.c. of a solution of Chlorine water ; the Iodine liberated was completely decolorized by the addition of 22.5 c.c. of a solution of Sodium Thiosulphate containing 1.58 grams of $\text{Na}_2\text{S}_2\text{O}_3$ per litre. Find the strength of the Chlorine solution in grams per litre.

PRACTICAL EXERCISES.

To convert Copper into Cuprous Sulphide and to calculate a value of the Equivalent of Sulphur from the result. Weigh out accurately about 1 gram of clean Copper filings into a porcelain crucible. Add a little powdered Sulphur and heat over the bunsen flame. Combination occurs between the two elements ; burn away the excess of Sulphur, allow the contents of the crucible to cool and weigh. Add more Sulphur, reheat, burn off excess of Sulphur and weigh again. Repeat these processes till the weight is constant. The increase is the weight of Sulphur which has combined with the known weight of Copper.

In Cuprous compounds, the equivalent of Copper is 63. Using this fact, calculate the equivalent of Sulphur from the results of the experiment.

To prepare the Allotropic Varieties of Sulphur and to prove that each consists of Sulphur and nothing else. Prepare monoclinic crystals of Sulphur by melting yellow rhombic Sulphur in a porcelain dish and allowing it to cool. When a crust begins to form on the surface, pour away the still molten liquid and monoclinic crystals remain behind.

Prepare plastic Sulphur by pouring boiling Sulphur into cold water.

Weigh out 1 gram of monoclinic and of plastic Sulphur in a watch glass. Leave for 24 hours, when they will have changed back to rhombic Sulphur. Weigh again and note that there is no change in weight.

Perform the experiment described on page 217 of burning a known small weight of each of the three varieties in a stream of Oxygen, and weighing the Sulphur Dioxide produced.

To prepare Sulphuretted Hydrogen from its elements. Take some yellow Sulphur in a boiling tube, fitted with a cork and tubing as in the diagram

(Fig. 74). Heat the Sulphur to its boiling point, and then pass Hydrogen gas through the tube *A*, which dips under the surface of the molten Sulphur. Test the gas which issues at *B* for Sulphuretted Hydrogen by holding in it a piece of filter paper which has been dipped in Lead Acetate solution.

To prove that Sulphuretted Hydrogen Gas contains its own volume of Hydrogen. Use an apparatus set up as in the diagram (Fig. 75). A small piece of Tin is placed in the bulbous part of the tube and a small amount of Mercury in the bottom of the U-tube. Dry Sulphuretted Hydrogen must be passed

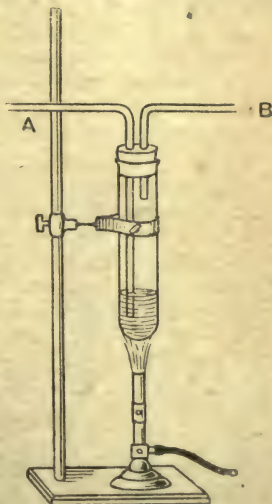


FIG. 74.—The synthesis of Sulphuretted Hydrogen.

through the apparatus till it has driven out all the air. Then the stop cock is closed and more Mercury poured into the U-tube till it occupies 10 cm. in each limb. Open the stop cock for one moment to equalize the pressure, and make the heights of the Mercury equal in the two limbs.

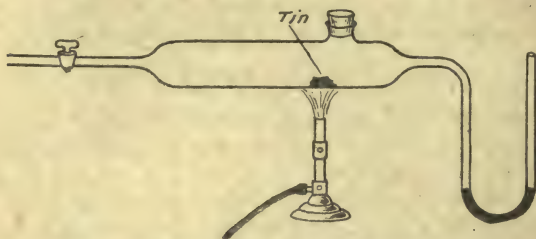
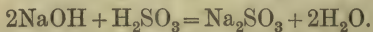


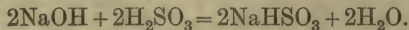
FIG. 75.—The composition of Sulphuretted Hydrogen.

Warm the Tin till it melts, and it will then absorb the Sulphur from the Sulphuretted Hydrogen. When the apparatus is quite cool again, the levels of Mercury in the U-tube will be found to be again equal, proving that the same volume of gas is left behind as was present at the start of the experiment. The residual gas may be shewn to be Hydrogen by the usual tests.

To prepare Sodium Sulphite and Sodium Bisulphite. Make a solution of Sulphurous acid by passing SO_2 through water; place this solution in a burette. Take 25 c.c. of a solution of Caustic Soda in a beaker; add the Sulphurous acid till neutral. Evaporate the solution down and allow to crystallize. The crystals are those of Sodium Sulphite :



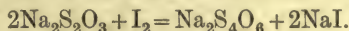
Take another 25 c.c. of the same Caustic Soda solution and add exactly twice as much Sulphurous acid. Crystallize either by evaporating at ordinary temperatures or by adding Alcohol. The crystals are those of Sodium Bisulphite :



To prepare Crystals of Sodium Thiosulphate. Make a strong

solution of Sodium Sulphite in water: add 10 grams of flowers of Sulphur and boil the liquid gently for 15 minutes. Filter away from the unabsorbed Sulphur and crystallize the filtrate. The crystals are those of Sodium Thiosulphate (Hypo).

Estimation of free Iodine by Sodium Thiosulphate Solution. When Sodium Thiosulphate comes into contact with *free* Iodine, reaction takes place according to the equation



Sodium Tetrathionate and Sodium Iodide, both colourless bodies in solution, are formed so that the yellow colour of the Iodine is destroyed.

This reaction forms a convenient method for determining, volumetrically, the quantity of free Iodine present in solution.

From the equation it is seen that 158 grams of Sodium Thiosulphate, *i.e.* 248 grams of the crystalline salt $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, react with 127 grams of Iodine. Make, therefore, a standard solution of Thiosulphate of Soda by dissolving 24.8 grams of the recrystallized salt in a litre of water. Every c.c. of this solution is equivalent to .0127 gram of Iodine.

In performing the titration, take 25 c.c. of the solution containing free Iodine in a *large* flask, and add distilled water till the flask is half full. Add, from a burette, the solution of Thiosulphate till the yellow colour of the Iodine has very nearly disappeared, and then add to the solution a few c.c. of freshly prepared Starch solution to act as an indicator.

Then continue to add the Thiosulphate solution drop by drop, till the blue colour of the "Iodide of Starch" disappears with the addition of one drop. Take care to shake the liquid in the flask well after every addition of Thiosulphate.

Then, from the number of c.c. of Thiosulphate solution added, the weight of *free* Iodine in the liquid can be readily calculated.

To use Sodium Thiosulphate to find the available amount of Chlorine in Bleaching Powder. Take 10 grams weight of fresh Bleaching Powder, digest with distilled water in a mortar, pour off the solution into a litre flask, and digest

with more water. Do this till all the soluble Hypochlorite is extracted, and then fill up the litre flask to the mark with distilled water.

Take 25 c.c. of this solution, acidulate with dilute Hydrochloric acid, and add to it excess of a solution of Potassium Iodide. Free Iodine is liberated by the available Chlorine, and its amount may be found by titration with Sodium Thiosulphate as indicated above.

Since 35.5 grams of Chlorine are equivalent to 127 grams of Iodine, the weight of available Chlorine present in the quantity titrated, and hence in the original Bleaching Powder, can readily be calculated.

To prepare Sulphuric Acid from Sulphur Dioxide. Use a large dry flat-bottomed flask of about 500 c.c. capacity. Fill it by downward displacement with Sulphur Dioxide gas either from a syphon containing liquid Sulphur Dioxide or by burning Sulphur in a current of air. Then add into the flask 2 or 3 drops of concentrated Nitric acid. Note the appearance and disappearance of the brown Nitrogen Peroxide fumes and the formation of "chamber crystals." Add a few more drops of Nitric acid and then dissolve the "chamber crystals" in about 20 c.c. of water. Note the evolution of more brown fumes as the crystals dissolve, and test the liquid produced for Sulphuric acid (1) by litmus; (2) by writing with it on paper with a clean pen and then warming the paper; (3) by adding Barium Chloride solution.

To prepare a Specimen of Pyrosulphuric Acid. Fill up about one quarter of a $\frac{5}{8}$ -inch test tube with crystals of Ferrous Sulphate. Place it in a clamp with its mouth inclined slightly downwards. Fit over the open mouth a boiling tube to act as a condenser and heat the Ferrous Sulphate strongly. Test the liquid which distils over for Sulphuric acid.

CHAPTER XX.

NITROGEN AND ITS COMPOUNDS.

NITROGEN.

Symbol, N. Atomic Weight, 14.04. Molecular Weight, 28.08.

History. The discovery of Nitrogen gas is usually attributed to Rutherford (1772). He obtained it from air by allowing an animal to breathe in it; also by burning Phosphorus and Charcoal in it and washing out the Carbon Dioxide and other impurities formed with Caustic Potash or Lime water. He called it "mephitic air," from its inability to support life; for a similar reason Lavoisier named it "azote." Its present name Nitrogen is due to its presence in Nitre.

Occurrence. Nitrogen, as has already been seen, is present in the free state in the atmosphere. It exists, combined as Ammonia or Ammonium salts, in many animal and vegetable compounds, and as Nitrates in *Saltpetre* or Nitre, KNO_3 , and *Chili Saltpetre*, NaNO_3 .

Preparation. It is easily obtained from the air by abstracting the Oxygen and other substances present. This may be done by burning Phosphorus or Sulphur in an enclosed space containing air over water and allowing the fumes which are formed to dissolve, but it is best obtained by forcing purified air slowly over red-hot Copper, which forms black Copper Oxide, CuO , with the Oxygen.

The air is forced slowly from a large container (Fig. 76) by means of water; it is purified from Carbon Dioxide by Caustic Potash and dried by strong Sulphuric acid, and then passes

over a thin spiral wire of Copper contained in a combustion tube, heated to redness in a furnace. Nitrogen passes on and may be collected over Mercury.

The Nitrogen obtained from air is never pure, as it contains about 1 per cent. of Argon and other gases.

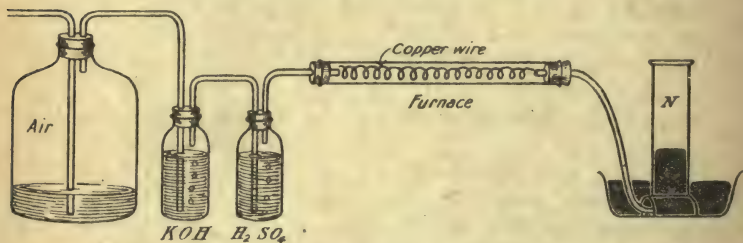
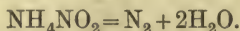
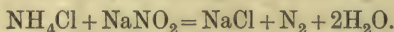


FIG. 76.—Preparation of Nitrogen from air.

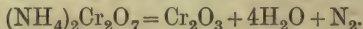
Pure Nitrogen is obtained by boiling a strong solution of Ammonium Nitrite. This substance splits up at once into Nitrogen gas and Steam :



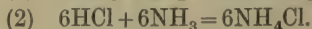
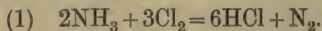
A mixture of Ammonium Chloride and Sodium Nitrite is often used instead of the Ammonium Nitrite :



Nitrogen gas is also evolved when the solid Ammonium Bichromate is heated. The reaction proceeds with some violence, a large quantity of green powder, Chromium Oxide, being formed, and Nitrogen gas evolved along with Steam :



The gas may also be prepared by passing Chlorine gas into a strong solution of Ammonia gas in water. The Chlorine unites with the Hydrogen of the Ammonia, forming Hydrochloric acid, which is neutralized by the excess of Ammonia to form Ammonium Chloride :



Great care must be exercised in performing this experiment, as, unless excess of Ammonia is present, a very explosive compound of Nitrogen and Chlorine called Nitrogen Trichloride, NCl_3 , is formed.

Properties. Nitrogen is a colourless odourless gas, only slightly soluble in water; 100 c.c. of water absorb 2.4 c.c. of Nitrogen at 0°C . It can be condensed to a colourless liquid which boils at -195°C ., and at -214°C . becomes a white snow-like solid.

It does not support life, but is not poisonous, as men and animals take it regularly into their lungs.

Nitrogen itself is a very inert gas and combines directly with very few other elements, whilst, in combination, it forms many unstable and often explosive compounds owing to the weakness with which it is held in combination. This may be expressed by saying that the atoms of Nitrogen are fonder of one another than of any other atom. At very high temperatures it may be made to combine with Oxygen (p. 259), and at moderate temperatures— 700°C .—with the metals Magnesium and Calcium, forming their respective Nitrides.

The absorption of Nitrogen gas by heated Magnesium may be shewn by means of the apparatus in the diagram (Fig. 77). The bulb *A* has Magnesium in it, and is filled with Nitrogen gas through the stop-cock *B*. It is made of hard glass, and can therefore be very strongly heated by means of a Meker

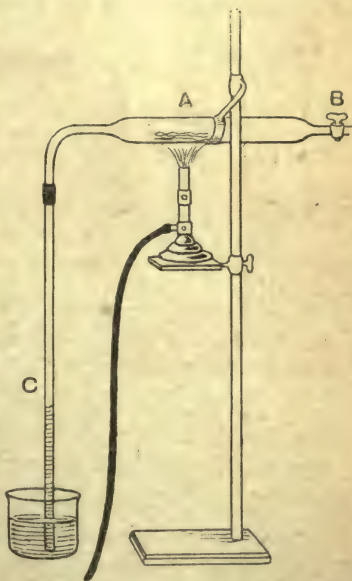


FIG. 77.—Absorption of Nitrogen by Magnesium.

burner or a blowpipe. When the expansion of the Nitrogen due to rise of temperature ceases, the liquid (coloured water) in the tube *C* is seen to rise owing to absorption of Nitrogen by the Magnesium. The Magnesium Nitride formed has a formula Mg_3N_2 .

NITROGEN AND HYDROGEN.

Nitrogen forms three compounds with Hydrogen, Ammonia NH_3 , Hydrazine, N_2H_4 or $(NH_2)_2$ and Hydrazoic acid, N_3H . Of these Ammonia is by far the most important, and will be the only one considered.

AMMONIA.

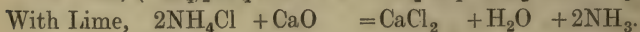
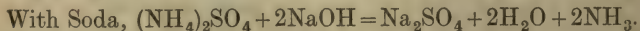
Formula, NH_3 . Molecular Weight, 17.04. Density, 8.52.

History. Ammonia gas and Ammonium compounds have been known from the earliest times; Glauber was probably acquainted with Ammonium Chloride (Sal-ammoniac), which he called Sal-armoniacum. The solution of the gas in water was obtained by distilling the hoofs and horns of animals, hence the name *Spirits of hartshorn*, under which it is still sold by chemists.

Its actual discovery and recognition were due to Priestley (1774), who got it by heating a mixture of Lime and Sal-ammoniac. He called it Alkaline Air.

Occurrence. It is found in small quantities in air, its presence being due to the putrefaction of animal and vegetable refuse. Its readily recognizable smell is noticed in stables, where it is evolved by the stale urine. Ammonium Chloride and Sulphate are found near volcanic vents, and are evidently produced from the gases evolved.

Preparation. Ammonia gas is produced when any Ammonium salt is heated with a strong base or alkali, such as Caustic Soda or Potash, or Lime.



The usual method for laboratory use is the latter. The apparatus used is fitted up as in the diagram (Fig. 78).

Since Water, in which the gas is very soluble, is produced during the reaction, the gas must be dried before the Water condenses if possible. The common drying agents, Sulphuric acid, Phosphorus Pentoxide, and Calcium Chloride are useless, the two former because they combine with Ammonia, forming Ammonium Sulphate and Phosphate, and the last-named because it absorbs it, forming a compound $\text{CaCl}_2 \cdot 8\text{NH}_3$. Lime

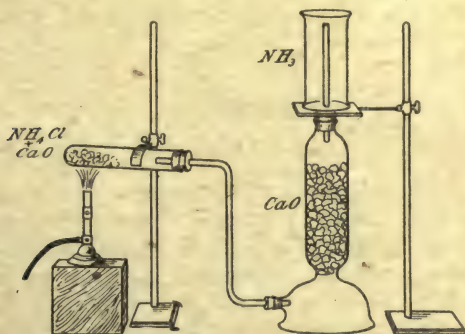
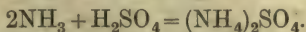


FIG. 78.—Preparation of Ammonia gas.

or Soda-Lime (a mixture of Lime and Caustic Soda) is therefore used as the desiccating agent, and the gas is collected by upward displacement or over Mercury.

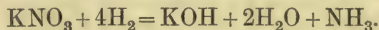
Ammonia is obtained commercially from the ammoniacal liquor formed as a bye-product in the manufacture of coal gas. This liquid is mixed with Milk of Lime and boiled, the evolved Ammonia being led into dilute Sulphuric acid, which absorbs it, forming Ammonium Sulphate :



The salt is obtained from the liquid by crystallization, and from it, if required, Ammonia gas can be driven off by heating with Lime, and, when absorbed in water, forms the Liquor Ammoniae of commerce.

Ammonia is also formed by the action of nascent Hydrogen upon any Nitrate (or Nitric acid). To obtain the gas itself the Hydrogen must be made in the liquid by an alkaline, not an acid, reaction.

Powdered Zinc and Caustic Soda are used, and when these are mixed with any Nitrate, *e.g.* Saltpetre, Ammonia gas is evolved on gently warming the liquid :



When a mixture of Nitrogen and Hydrogen, in the proportion of 1 : 3, is subjected to a series of electric sparks, a small amount of combination takes place, and about 2 per cent. of Ammonia is formed. A similar result occurs from the passage of sparks through pure Ammonia gas, 98 per cent. decomposing. If, however, the 2 per cent. of Ammonia is removed as soon as it is formed, by water, more Nitrogen and Hydrogen combine, and eventually the whole of the gases can be caused to unite, forming Ammonia.

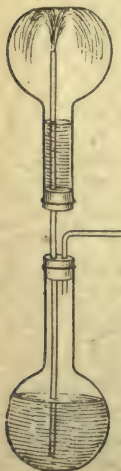


FIG. 79.—To shew the solubility of Ammonia gas.

Properties. Ammonia is a colourless gas, with a very pungent smell. Its vapour, in small quantities, brings tears to the eyes, but, in large quantities, it causes suffocation. It is much lighter than air.

Ammonia gas is extremely soluble in water. At 0° C. 1 c.c. of water absorbs 1148 c.c. of the gas, and at ordinary temperatures about 800 c.c. are absorbed.

Its great solubility may be well shewn by filling a round-bottomed flask with the gas, and placing it over another flask fitted with tubes as in the diagram (Fig. 79), and containing red litmus solution. If a few drops of litmus are forced into the upper flask the whole of the Ammonia dissolves, and the pressure of the air drives the rest of the litmus into the vacuum thus formed, in the form of a fountain. At the same time, the red litmus

is turned blue owing to the alkaline nature of the solution of Ammonia.

During the process of solution, a certain amount of heat is liberated, and, consequently, when the gas is driven out of the solution, a corresponding amount of cold is produced. This is well shewn by placing about 20 c.c. of strong Ammonia solution in a beaker standing in a few drops of water on a wooden board. When air is blown rapidly through the liquid, the Ammonia gas is liberated, and the cold produced is quite sufficient to freeze the water and cause the beaker to adhere strongly to the board.

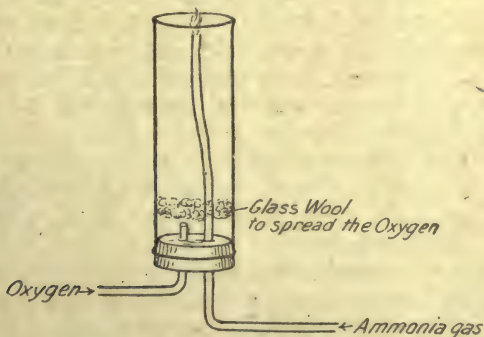


FIG. 80.—Combustion of Ammonia gas in Oxygen.

Ammonia gas is easily liquefied. At 0° C. a pressure of 4.2 atmospheres will liquefy it. Liquid Ammonia boils at -33° C. Faraday liquefied it first by heating a compound of Ammonia and Silver Chloride in one limb of one of his tubes (Fig. 50), the other limb being cooled in a freezing mixture.

Liquid Ammonia is largely used in the artificial production of ice by Carré's process.

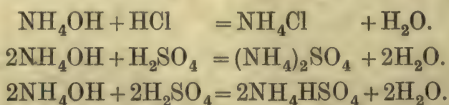
Ammonia gas does not burn in air, though it tinges with yellow a bunsen flame into which a jet is led. It can, however, be made to burn readily in a stream of Oxygen gas, by using an apparatus similar to the one in the diagram (Fig. 80).

Nitrogen and Water are the principal products of the combustion.

The action of Chlorine on Ammonia has already been studied. A similar action occurs with Iodine, producing a chocolate-coloured amorphous powder called Nitrogen Iodide, to which the formula NI_3 was assigned. It has lately been discovered that this formula is wrong, and that the compound is a mixture of the Tri-iodide and Ammonia, and has a formula $\text{N}_2\text{H}_3\text{I}_3$, $(\text{NI}_3 \cdot \text{NH}_3)$. When dry it is a most unstable substance, and consequently highly explosive. It has been stated that it explodes with the walking of a fly over the dry powder.

The solution of Ammonia gas in water possesses strong Basic properties; it turns red litmus blue, yellow turmeric brown, and neutralizes acids. The solution, on this account, is often spoken of as Ammonium Hydrate, and its formula is written NH_4OH to correspond with the alkalies Caustic Soda, NaOH and Caustic Potash, KOH . With acids this solution forms substances which are crystalline, and possess all the properties of salts. They are reckoned as being salts of a hypothetical radicle, Ammonium, NH_4 , which is mono-valent and its compounds resemble those of Sodium and Potassium.

The formation of the Chloride and Sulphates of Ammonium is shewn by the equations:



Composition and Formula. That Ammonia gas contains Nitrogen and Hydrogen may be best shewn by passing the thoroughly dried gas over red-hot Copper Oxide (Fig. 81). A liquid which may be readily identified as Water collects in the cooled U-tube and, as Water contains Hydrogen, this element must be present in Ammonia, as there is none in Copper Oxide; whilst a gas which answers the tests for Nitrogen collects in the test tube, and this gas can only have come from the Ammonia.

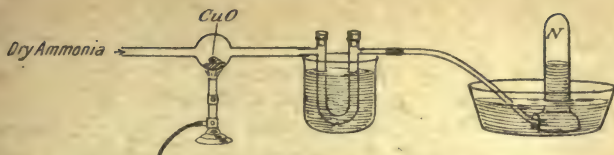


FIG. 81.—Experiment to shew that Ammonia gas contains Nitrogen and Hydrogen.

To determine the proportion of Nitrogen to Hydrogen, a further experiment is made. The tube *A* (Fig. 82) is filled with dry Chlorine gas, and through the cork which fits its open end is fitted a dropping funnel *B* containing a saturated solution of Ammonia gas. This solution is allowed to fall drop by drop into the Chlorine. At first a flash of light marks the fall of each drop, but this soon ceases, and the action between the Chlorine and the Ammonia is finished. Then the Ammonia liquor in *B* is replaced by dilute Sulphuric acid, which is carefully run into the tube to neutralize any excess of Ammonia which may have been added, and this acid solution is allowed to go in as long as it will, *i.e.* till the pressure inside is equal to the pressure of the atmosphere outside. It is then found that the Nitrogen remaining in the tube occupies precisely one-third of the whole tube.

Now the Hydrogen in the Ammonia has combined with the Chlorine, and in equal quantities by volume. Hence a tube full of Hydrogen must have been associated with $\frac{1}{3}$ tube full of Nitrogen in the Ammonia which was decomposed, that is, in Ammonia, $N : H :: 1 : 3$, and its formula is consequently $(NH_3)_x$.



FIG. 82.—Composition of Ammonia.

By a further experiment, the density of Ammonia gas is found to be 8.5 ($H=1$). Hence its molecular weight is 17.

Whence $(NH_3)_x = 17$, i.e. $(14+3)x=17$ and $x=1$, giving the correct formula as NH_3 .

Uses. Ammonia gas is used to a great extent in the artificial production of ice; as a cleanser, on account of its solvent power for grease and fat; in smelling salts, where its stimulating action often produces the desired effect; and in the manufacture of Washing Soda by the Solvay process (p. 385).

OXIDES AND OXY-ACIDS OF NITROGEN.

Nitrogen forms five compounds with Oxygen:

- (1) Nitrous* Oxide (Hyponitrous Anhydride) - N_2O .
- (2) Nitric Oxide - - - - - NO .
- (3) Nitrogen Trioxide (Nitrous Anhydride) - N_2O_3 (?).
- (4) Nitrogen Peroxide - - - - - NO_2 .
- (5) Nitrogen Pentoxide (Nitric Anhydride) - N_2O_5 .

Three Oxy-acids of Nitrogen are known, being solutions in water of three of the above Oxides:

Hyponitrous acid (from N_2O)	-	-	-	HNO .
Nitrous acid (from N_2O_3)	-	-	-	HNO_2 .
Nitric acid (from N_2O_5)	-	-	-	HNO_3 .

By far the most important of these compounds is Nitric acid, and as, from it, most of the others are prepared, directly or indirectly, it will be considered first.

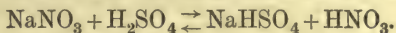
NITRIC ACID.

Formula, HNO_3 . Molecular Weight, 63.05.

History. Nitric acid has been known from very early times. Geber prepared it by distilling a mixture of Copperas (Ferrous Sulphate), Saltpetre (Potassium Nitrate) and Alum. He called it *aqua fortis*, on account of its strong solvent properties.

Glauber (1650) made it, by the method still employed, of distilling Saltpetre with oil of Vitriol. Its composition was not known till Lavoisier (1776) found out that it contained Oxygen, and later (1784) Cavendish proved that it contained Hydrogen, Nitrogen and Oxygen.

Preparation. Nitric acid is driven off when any Nitrate is heated with strong Sulphuric acid. Sodium and Potassium Nitrates, being cheap, are usually employed. With Sodium Nitrate the reaction may be represented thus :



At ordinary temperatures all four substances are represented in the liquid formed. Nitric acid boils at 86°C . and Sulphuric

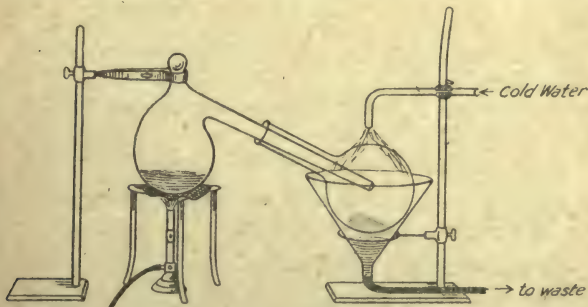
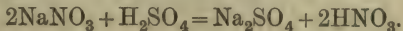


FIG. 83.—Preparation of Nitric Acid.

acid at 330°C ., Sodium Nitrate and Sodium Hydrogen Sulphate have very high boiling points, so that on heating to about 100°C ., the most volatile substance present, Nitric acid, vaporizes, distils off and may be condensed in a suitable apparatus such as the one shewn in the diagram (Fig. 83).

At higher temperatures, with less Sulphuric acid and more of the Nitrate, the Normal Sodium Sulphate is formed, though the Nitric acid is liable to be decomposed :



Nitric acid prepared in this way always contains some of the reddish brown gas (mainly Nitrogen Peroxide), which is

seen in the retort and the receiving flask, and has consequently a yellow colour. On boiling the gas is driven off and pure colourless Nitric acid is left.

Cavendish prepared Nitric acid, at first unwittingly, by passing an electric spark through a mixture of Oxygen and Hydrogen containing a little Nitrogen; the water produced by the explosion has acid properties; in fact, contains Nitric acid.

Its manufacture from air will be considered later (p. 259).

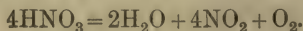
Properties. Nitric acid is a colourless liquid, of density 1.53. It has a strong choking smell and fumes in the air. It mixes in all proportions with water and, as with Sulphuric acid, heat is evolved, and contraction in volume occurs on



FIG. 84.—Decomposition of Nitric Acid.

mixing. The pure acid boils at 86° , and at the same time begins to decompose into Water, Nitrogen Peroxide and Oxygen. This evidently makes the acid weaker in strength, and the boiling point rises gradually up to 120.5° C., when an acid containing 68 per cent. of Nitric acid distils over unchanged. On the other hand, a weaker solution than 68 per cent. boils below 120.5° , but the boiling point gradually rises to that temperature, and then a 68 per cent. acid distils over unchanged (cp. Hydrochloric acid, p. 190).

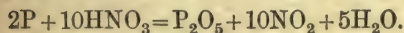
The decomposition mentioned above commences below the boiling point of the acid, and is very marked at high temperatures. If the concentrated acid is placed in the bowl of a churchwarden clay pipe, the stem of which is made red hot, Oxygen can be collected from the products of decomposition (Fig. 84). The reaction is represented thus:



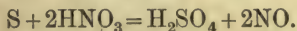
The red Nitrogen Peroxide fumes which are formed dissolve in the water.

Nitric Acid as an Oxidizing Agent. On account of the comparative ease with which Nitric acid splits off part of its Oxygen (*N.B.* two molecules of acid yield one atom of Oxygen), it is a powerful oxidizing agent.

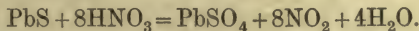
Phosphorus, if lighted and plunged into a flask full of Nitric acid vapour (Fig. 85), burns with a brilliant light, forming white fumes of Phosphorus Pentoxide and red fumes of Nitrogen Peroxide :



If red Phosphorus is boiled with the concentrated acid, Phosphoric acid, H_3PO_4 , is formed. Similarly Sulphur yields Sulphuric acid :

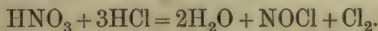


It oxidizes also Arsenious Oxide, As_2O_3 , to Arsenic Oxide, As_2O_5 , Ferrous salts to Ferric salts, and many metallic Sulphides when boiled with it are changed into Sulphates, *e.g.*



Aqua Regia. A mixture of Hydrochloric and Nitric acids in the proportion of 3 : 1 was called by the old alchemists Aqua Regia because of its power to dissolve Gold—the king of metals.

This power is probably due to the formation of nascent Chlorine by the interaction of the two acids, thus :



The Chlorine attacks Gold and Platinum, forming their Chlorides, $AuCl_3$ and $PtCl_4$.

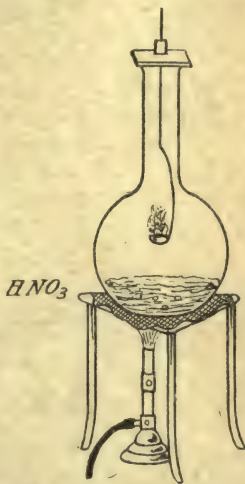
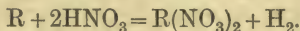


FIG. 85.—Burning of Phosphorus in Nitric Acid vapour.

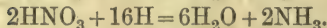
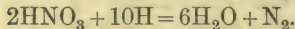
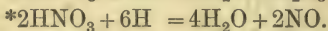
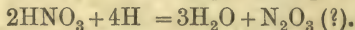
Action on Metals. The results of the action of Nitric acid on metals are complicated by secondary reactions.

It is probable that Hydrogen is first liberated, *e.g.* for a di-valent metal R :

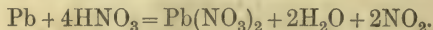


Then the "nascent" Hydrogen attacks the excess of Nitric acid present, reducing it to one of the Oxides of Nitrogen or to Nitrogen itself; even, in some cases, to Ammonia.

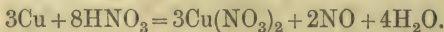
These reductions are seen in the following equations :



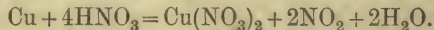
The two most common reactions are those marked with an asterisk. For instance, with Lead,



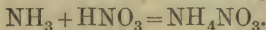
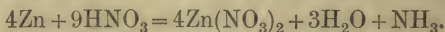
With Copper, when the acid is dilute, the action is



But strong acid acts thus :



Dilute acid and Zinc yield Nitrous Oxide mainly, but a strong acid yields Ammonia, which, of course, combines with excess of acid to form Ammonium Nitrate :



Formula of Nitric Acid. The structural formula of Nitric acid is usually written $\begin{array}{c} O \\ \parallel \\ N-O-H \\ \parallel \\ O \end{array}$, in which Nitrogen is reckoned as penta-valent. This agrees with the mono-basic

properties of the acid and with the ease with which it yields Nitrogen Peroxide, NO_2 .

Nitrates. Nitric acid forms a very important series of salts with bases which are called Nitrates. Since the acid is mono-basic, there are no Hydrogen Nitrates, as there is only one Hydrogen atom in the molecule of the acid.

Nitrates are all of them soluble in water, and are readily prepared by dissolving the corresponding bases in dilute Nitric acid and crystallizing from the solutions thus obtained.

Like the acid, most of the Nitrates decompose readily on heating, splitting off Oxygen, *e.g.*

For Potassium Nitrate, $2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2$.

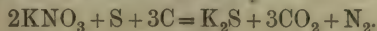
For Lead Nitrate, $2\text{Pb}(\text{NO}_3)_2 = 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$.

For this reason, and also because they are solids, Nitrates are largely used for explosives and fireworks, being mixed with various combustible bodies such as Charcoal, Sulphur, Iron, etc. The gorgeous "star" effects are produced by burning finely divided Iron; red and green fires by using the Nitrates of Strontium and Barium, etc.

Explosives. The function of an explosive is to produce a large volume of gas from a very small volume of original substance, be it solid or liquid. To produce this effect various substances are burnt, such that the products of combustion are gaseous, and these gaseous products are expanded very greatly by the heat produced during the combustion. To make the explosion, this expansion must be produced very suddenly. So, the combustible substance and the supporter of combustion are very intimately mixed together, so that the whole mass takes fire at once.

Gunpowder consists of an intimate mixture of Potassium Nitrate, Sulphur and Charcoal in the proportions 75 : 10 : 15.

Theoretically, combustion in these proportions of the constituents would take place on the lines of the equation



As a matter of fact, the resulting products are much more complex, for, as well as those given in the above equation,
o.c. R

solids such as Potassium Carbonate and Sulphate, and gases, Carbon Monoxide and Sulphuretted Hydrogen, are formed at the end of the reaction.

For both sporting and war purposes, the solid products are bad because of the smoke produced, so that gunpowder is very little used nowadays, its place being taken by smokeless powders, which are all products of Nitric acid.

Nitrocellulose is one of the most important of these. Commonly called Guncotton, it is made by soaking cotton wool in a mixture of Nitric and Sulphuric acids—the latter to absorb the Water formed during the reaction—for several hours, washing the resultant product to get rid of every trace of acid and drying it.

It then resembles the original cotton-wool in appearance, but is really Hexa-nitro-cellulose, $C_{12}H_{14}O_{10}(NO_2)_6$ in composition, and the products of its detonation are all gaseous, and therefore no smoke is produced.

Nitroglycerin is another high explosive produced by the action of Nitric and Sulphuric acids on Glycerin. In composition it is Glyceryl Tri-nitrate, $C_3H_5(NO_3)_3$, and in the pure state is a liquid. It is a highly unstable compound, and explodes when subjected to a very small amount of friction. For practical purposes it is mixed with Nitro-cellulose and vaseline to form *Cordite* and, soaked into a pumice-like earth—Kieselguhr—it forms *Dynamite*. By this means its sensitiveness is somewhat tamed.

Picric acid, a nitro-derivative of Carboic acid or Phenol, is the principal constituent of *Lyddite* and *Melinite*.

Nitrogen in Nature. All living matter, whether animal or vegetable, contains Nitrogen; it is absolutely essential for its growth. When it decays, part of the Nitrogen goes into the atmosphere and part goes into the soil, and is absorbed by plants. Neither animals nor plants can absorb free Nitrogen directly from air, so that part is apparently lost steadily, and more has to be taken from the ground, in combined form, by the plants. This gradually impoverishes the soil, and its loss must therefore be made good by cultivation.

This takes the form of manuring the ground either with waste animal or vegetable tissues, or with what are called artificial manures which contain Nitrogen in combined form, either as soluble Nitrates, such as those of Potassium, Sodium, or Calcium, or as salts of Ammonium.

There is, however, a certain order of plants, called *leguminosae*—peas, beans, clover, etc.—which appears to live in a kind of partnership—symbiosis it is called by biologists—with a species of bacteria. The bacteria live, as guests, in nodules on the root fibres of their hosts, and have the power of converting the Nitrogen of the atmosphere into a form available as food for the plants in which they live.

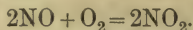
These plants, then, can extract the Nitrogen for their growth from air, but they are a small minority, and all other cultivated plants require Nitrogen to be applied artificially. Now the supply of Nitrogen containing compounds in the Earth's crust is not unlimited; it has been calculated that even the vast deposits of Chili Saltpetre will be exhausted, at the present rate of consumption, in less than 100 years. In order, then, for the land to be kept fertile, some other source of Nitrogen must be found, and this, of course, is present, if it can be used, in the atmosphere.

Fixation of Atmospheric Nitrogen. Many attempts have been made to bring the free Nitrogen of the air into such a combination as to be available for plant food, but, up till comparatively recently, no commercial success was attained.

Cavendish (1785) proved that when electric sparks were passed through damp air, an acid was produced, and he identified the acid to be Nitric acid. But not till long afterwards was the cost of producing electricity, of sufficiently high power, cheap enough to produce the acid, and neutralize it to get it into solid form, at a price which would allow it to compete with the fertilizers found in nature.

Siemens and Halske (1902) passed air through a chamber containing an electric arc spread out fan-wise by means of an electromagnet. The apparatus is shewn diagrammatically in Fig. 86. Nitric Oxide (NO) was produced by the intense heat, and this is swept away from the arc before it has time

to dissociate into Nitrogen and Oxygen again. It is then mixed with more air, with the Oxygen of which it combines, forming Nitrogen Peroxide :



This gas is then led through towers, where it meets with water and Milk of Lime (Calcium Hydrate), with which it unites, forming the Nitrate and Nitrite of Calcium.

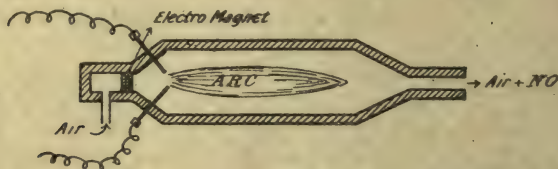
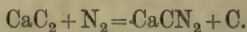


FIG. 86.—Siemens and Halske's Experiment.

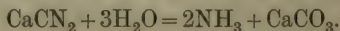
Norway, which has a great store of energy in its waterfalls, is a country where this process is largely adopted, and the resulting Norway Saltpetre, as it is called, is now sold in large quantities as a fertilizer.

Quite recently a new production has been brought out, also in Norway, called Nitrolime. Chemically this substance consists mainly of Calcium Cyanamide, CaCN_2 . It is obtained by heating finely powdered Calcium Carbide, CaC_2 , to a temperature of 1200°C . in a current of Nitrogen gas ; the following reaction takes place :



The Nitrogen is obtained in a fairly pure state, by the fractional distillation of liquid air (p. 179).

When Nitrolime is mixed with damp soil, it reacts with the moisture, forming Ammonia gas and Chalk :



The Ammonia is oxidized, as in the case of fresh stable manure, by the bacteria in the soil, to Nitrates, and is then readily absorbed by the plants.

NITROUS OXIDE.

Formula, N_2O . Molecular Weight, 44.08.

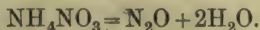
Preparation. Nitrous Oxide gas is produced when dilute Nitric acid acts upon the metals Zinc or Tin, but this method does not yield the pure gas by any means.

A better way is to heat crystals of Ammonium Nitrate, NH_4NO_3 , in a retort (Fig. 87) to a temperature of about



FIG. 87.—Preparation of Nitrous Oxide gas.

200° C., when the liquid Nitrate begins to decompose into Nitrous Oxide and Steam :



At 240° C. decomposition is so rapid as to be almost explosive, hence the use of a wide delivery tube as in the diagram, which permits the rapid egress of the gas. It must be collected over hot water, as it dissolves to some extent in cold water.

Impurities, by this process, are Nitrogen, Nitric Oxide, NO, and Nitrogen Peroxide, NO_2 . If the gas is wanted quite pure, for medical purposes, it must be first passed through Ferrous Sulphate solution to absorb the Nitric Oxide and then through Caustic Potash to absorb the Nitrogen Peroxide.

Properties. Nitrous Oxide is a colourless gas with a faint sweet smell. It is very heavy, its density being the same as

that of Carbon Dioxide. 100 c.c. of water at 0° C. dissolve 130 c.c. of Nitrous Oxide, and at 20° C., 67 c.c. Hence it is collected over hot water.

It is condensed to a liquid by a pressure of 30 atmospheres at a temperature of 0° C. This liquid is made in considerable quantities for dentists and doctors, on account of the fact that the Nitrous Oxide gas which is evolved when the pressure is released, when inhaled, produces unconsciousness and insensibility to pain. Long continued inhalation may produce death, whilst, in small quantities, it produces a sort of hysteria or intoxication. Hence the name of "Laughing-Gas," by which it is sometimes called.

Nitrous Oxide gas splits up with comparative ease into a mixture of 2 volumes of Nitrogen to 1 volume of Oxygen. This mixture resembles Air with a higher percentage of Oxygen, and it is therefore a better supporter of combustion than Air. The heat of a glowing splinter is sufficient to cause decomposition, and the splinter itself is rekindled. Feebly burning Sulphur is not able to decompose the gas, and so is extinguished, but brightly burning Sulphur, Phosphorus, and most other combustibles burn well in the gas, uniting with the Oxygen and leaving Nitrogen behind.

It is possible, therefore, to mistake this gas for Oxygen, but points of difference are seen in the smell, solubility in water and density; also in the fact that this gas does not turn Pyrogallic acid and Potash brown, nor does it form red fumes when mixed with Nitric Oxide gas, as Oxygen does.

Composition. The composition of Nitrous Oxide gas may be determined by means of the apparatus shewn in the diagram (Fig. 88). A measured quantity of the pure gas is drawn into the graduated tube *A*. This is then connected up as in the figure, and by raising the tube *D*, which is full of Mercury, the gas is forced through the narrow tube *B*, containing a spiral of thin Copper wire heated to redness. The gas passes over into *C*, and may be passed through *B* again by raising the tube *E*. This is done several times, till, finally, the Copper has withdrawn all the Oxygen from the gas and only Nitrogen is left.

The volume of this resultant Nitrogen is found, on cooling, to be exactly the same as that of the original Nitrous Oxide. Hence Nitrous Oxide contains its own volume of Nitrogen. By Avogadro's Law, 1 molecule of Nitrous Oxide contains 1 molecule of Nitrogen, *i.e.* N_2 , and its formula is N_2O_x .

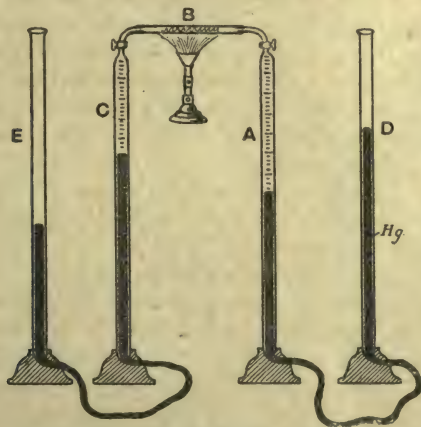


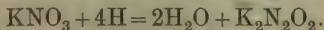
FIG. 88.—Composition of Nitrous Oxide gas.

The density of Nitrous Oxide ($H=1$) is found to be 22, which gives a molecular weight of 44.

Therefore $N_2O_x = 44$, whence $x=1$, and the formula is N_2O .

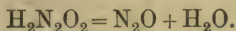
Hyponitrous Acid and the Hyponitrites. Nitrous Oxide gas may be regarded as the anhydride of an acid, which has itself not been isolated, but one or two of its salts have been prepared.

When a solution of Potassium Nitrate or Nitrite is reduced by nascent Hydrogen (Sodium amalgam and water is usually employed), a salt Potassium Hyponitrite, $K_2N_2O_2$, is formed, thus:



When the solution is acidified with Acetic acid (to get rid of the Alkali) and Silver Nitrate added, a yellow precipitate of Silver Hyponitrite, $Ag_2N_2O_2$, is formed.

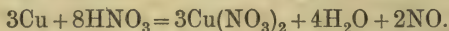
Attempts to isolate the acid have all failed, as it immediately splits up into Nitrous Oxide and Water :



NITRIC OXIDE.

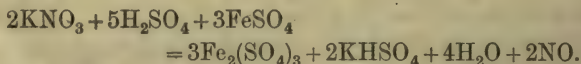
Formula, NO. Molecular Weight, 30.01.

Preparation. Nitric Oxide gas is the chief gas produced when dilute Nitric acid ($\text{HNO}_3 : \text{H}_2\text{O} :: 1 : 1$) is poured over Metallic Copper :



The apparatus used is a flask or Wolff's bottle, and the gas is collected over water ; no heat is required. As the action continues, the quantities of Nitrous Oxide gas and Nitrogen tend to increase, and, to get the pure gas, the mixture is led through a solution of Ferrous Sulphate, which absorbs the Nitric Oxide and Nitrogen Peroxide, but allows the other gases to pass through. Then, on boiling the Ferrous Sulphate, pure Nitric Oxide is evolved, the Nitrogen Peroxide being retained in combination.

A pure gas is obtained by acting upon a mixture of Potassium Nitrate and Ferrous Sulphate with Sulphuric acid ; the Ferrous Sulphate reduces the Nitric acid formed to Nitric Oxide :



Properties. It is a colourless gas, whose smell is unknown because, in contact with air, it immediately forms red fumes of Nitrogen Peroxide, with the evolution of a considerable amount of heat. If both gases are perfectly dry, this union of Nitric Oxide and Oxygen does not take place ; water is therefore a catalytic agent in the reaction.

It is not very soluble in water, 100 c.c. of water dissolve 4.6 c.c. of the gas at 20°C . It is very difficult indeed to liquefy, as the boiling point of the liquid is -150°C .

It is a much more stable compound than Nitrous Oxide ;

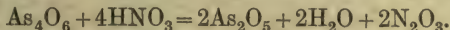
feebly burning Phosphorus is extinguished by it, but, if brightly alight, it splits the gas up into Nitrogen and Oxygen and burns with a brilliant flame. Nitric Oxide is not split up by the heat of a burning taper or burning Sulphur; in fact a bright red heat is necessary to make it decompose, and then only partial decomposition takes place.

The metals Potassium and Copper will absorb the Oxygen from Nitric Oxide when hot.

If a few drops of Carbon Disulphide, CS_2 , are shaken up with a jar full of Nitric Oxide and a light is applied to it, a very brilliant blue flame is produced, which is rich in actinic rays, and is consequently employed sometimes for photographic purposes.

Composition. By a precisely similar experiment to that used for Nitrous Oxide (p. 263), it is found that Nitric Oxide contains half its volume of Nitrogen, and hence its formula is NO_x . Its density is 15, and consequently its molecular weight 30, which gives $x=1$ and a formula of NO .

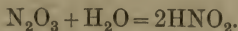
Nitrogen Trioxide, N_2O_3 . There is considerable doubt as to whether this compound exists. It is supposed to be evolved, as a reddish-brown gas, when Arsenious Oxide is treated with strong Nitric acid, according to the equation



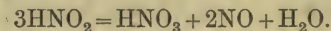
It has, however, been shewn that the gas given off under these conditions is a mixture of Nitric Oxide and Nitrogen Peroxide; $2\text{N}_2\text{O}_3$ being equal to $2\text{NO} + 2\text{NO}_2$. Later researches have shewn that there is a small percentage of N_2O_3 mixed with the NO and NO_2 given off in the reaction.

NITROUS ACID AND THE NITRITES.

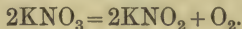
If Nitrogen Trioxide existed, another name for it would be Nitrous Anhydride, since its solution in water would yield an acid—Nitrous acid:



This acid is known, but only in dilute solutions, and, even then, it breaks up fairly rapidly into Nitric acid, Nitric Oxide and Water :



Its salts, which are called Nitrites, are stable substances, those of the alkali metals being obtained by fusing the Nitrates, which split off one atom of Oxygen :



At higher temperatures they themselves decompose. With dilute acids they evolve red Nitric fumes, and by this reaction are readily distinguished from Nitrates.

NITROGEN PEROXIDE.

Formula, N_2O_4 or NO_2 . Molecular Weight, 92.08 or 46.04.

Preparation. Nitrogen Peroxide is formed, as has already been seen, when one volume of Oxygen unites with two volumes of Nitric Oxide :

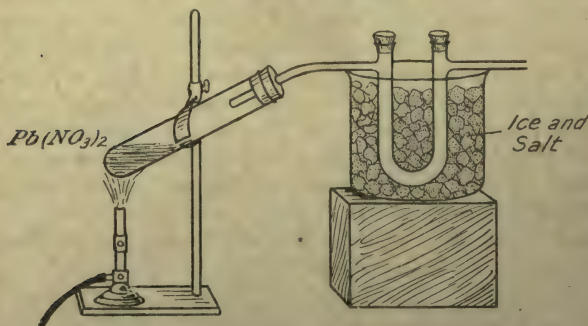
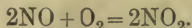
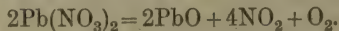


FIG. 89.—Preparation of Nitrogen Peroxide.

It is more readily prepared by heating one of the Nitrates of the heavy metals, *e.g.* Lead :



The evolved gases are led through a U-tube (Fig. 89) surrounded by a freezing mixture of ice and salt, and here the Nitrogen Peroxide is condensed to a liquid.

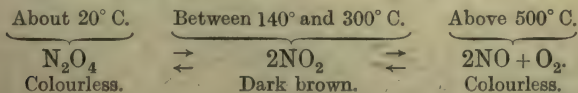
Action of Heat on Nitrogen Peroxide. At low temperatures Nitrogen Peroxide forms colourless crystals which melt at -9°C ., forming a colourless liquid. As the temperature rises, the liquid begins to acquire a colour, being distinctly yellow at 10°C . and orange at 15°C . At 26°C . it boils, and gives off a reddish-brown vapour. This vapour on further heating becomes darker and darker, being chocolate-coloured at 40°C ., whilst at 140°C . it is almost black.

These changes of colour in the vapour are accompanied by changes in density; at 27°C . its density ($H=1$) is 38.2, but this number gradually decreases with the temperature till, at 140°C ., it is 23 and remains constant for a considerable rise in temperature.

The explanation is that at 140°C . the gas consists entirely of molecules of NO_2 (density 23), but that, at lower temperatures, there is an admixture of molecules of N_2O_4 (density 46), the number increasing as the temperature diminishes, but, as the density never gets as high as 46, the gas is never pure N_2O_4 , but always a mixture of N_2O_4 and NO_2 molecules. This phenomenon, in which a substance, on heating, splits up into simpler molecules which recombine on cooling, is known as *Dissociation*, and is of fairly common occurrence in Chemistry.

At temperatures above 500°C . the dark brown NO_2 gas begins to get lighter in colour and in density, owing to its splitting up into Nitric Oxide and Oxygen, which are both colourless gases; this change also is reversible.

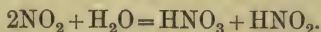
These changes of Nitrogen Peroxide under the influence of heat may be summarized thus:



Properties. Nitrogen Peroxide gas has a bad smell, in small quantities it produces headache and sickness, and in large quantities it is poisonous.

It will extinguish a lighted taper, but very brightly burning Phosphorus is capable of splitting it up. It is a good oxidizing agent; many metals, *e.g.* Potassium, Mercury, Copper, when heated in the gas, form their Oxides. It oxidizes Sulphur Dioxide to Sulphur Trioxide, as seen in the preparation of Sulphuric acid.

It is readily soluble in water, a mixture of Nitrous and Nitric acids being formed at low temperatures:

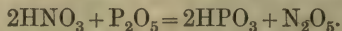


Priestley (1772) used the fact that this gas, which is soluble in water, is formed when Nitric Oxide is mixed with air, to determine the percentage of Oxygen in air. Nitric Oxide is gradually admitted to air contained in a vessel over water, so that the red fumes dissolve as soon as they are formed. The moment the formation of red fumes ceases, the admission of Nitric Oxide is stopped, and the resultant Nitrogen measured.

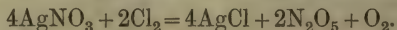
NITROGEN PENTOXIDE.

Formula, N_2O_5 . Molecular Weight, 108.03.

Preparation. When concentrated Nitric acid is gradually mixed with Phosphorus Pentoxide, and the mixture is kept quite cool, a pasty mass is obtained, from which Nitrogen Pentoxide can be obtained by distillation as a colourless liquid, which forms, almost at once, white crystals in the receiver:



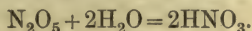
Deville (1849), who discovered this substance, obtained it by passing dry Chlorine gas over dry Silver Nitrate contained in a U-tube, which was kept cool by being immersed in water:



Properties. Nitrogen Pentoxide occurs as brilliant white prismatic crystals, which melt at 30°C . with some decomposition. At 45°C . to 50°C . decomposition into Nitrogen Peroxide and Oxygen is complete, and, when suddenly heated

to higher temperatures, this decomposition takes place with explosive violence.

Nitrogen Pentoxide absorbs water very readily and dissolves in it with the evolution of great heat, forming Nitric acid; on this account it is called Nitric Anhydride:



PROBLEMS.

53. 5 grams of Sal Ammoniac are mixed with Lime and heated; the gas evolved is led into Nitric acid. Calculate the weight of Ammonium Nitrate formed.

54. 1.5 grams of Ammonium Sulphate are boiled with Caustic Potash, and the Ammonia evolved is led into 50 c.c. of N. HCl. This latter solution required 27.3 c.c. of N. KOH to complete the neutralization. Find the percentage of Ammonia in Ammonium Sulphate (see p. 271).

55. 450 c.c. of Ammonia gas, measured at 15° and 775 mm., are led into dilute Sulphuric acid, and the liquid is evaporated to dryness. What weight of Ammonium Sulphate is formed?

56. Calculate the weight of a litre of a mixture of Nitrogen and Hydrogen in the proportion 1 : 3, and compare it with the weight of a litre of Ammonia gas, both gases being measured at 0° C. and 760 mm.

57. 80 c.c. of Air is taken in a jar over water, Nitric Oxide is added till no more red fumes appear. It is found that 33 c.c. of Nitric Oxide are required. Determine the percentage of Oxygen in air.

PRACTICAL EXERCISES.

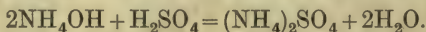
To determine the effect of heat upon Ammonium Dichromate. Fit an ordinary test tube with a cork and single delivery tube, dipping under water. Place in it a *small* quantity of solid Ammonium Dichromate. Heat gently, notice the rapid decomposition and collect the gas evolved in a test tube. Apply to this gas the tests for Nitrogen. The green solid left in the tube is Chromium Trioxide, Cr_2O_3 .

To prepare Ammonia Gas from Saltpetre. Take a little solid Saltpetre in a boiling tube; add to it some Zinc powder and 20 c.c. of Caustic Soda solution. Warm gently till a gas is evolved, and test this gas for Ammonia, (1) by its odour;

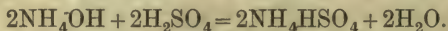
(2) by red litmus paper; (3) by holding in it the stopper of the Hydrochloric acid bottle.

To notice the cold produced by blowing Air through a Solution of Ammonia. Take 20 c.c. of Ammon. Fortiss. in a beaker; stand the beaker in 2 or 3 drops of water placed on a wooden block, and blow a stream of air through the solution by means of bellows. As the Ammonia gas is driven off, enough heat is absorbed to freeze the water, and the beaker is frozen to the wooden block.

To prepare the two Sulphates of Ammonium. Titrate 25 c.c. of a fairly dilute solution of Ammonia with dilute Sulphuric acid, using litmus as an indicator. The neutral liquid will deposit crystals of Ammonium Sulphate when concentrated:



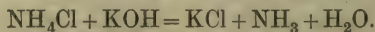
Take another 25 c.c. of the same Ammonia solution, and add exactly twice the amount of the same Sulphuric acid solution as was added in the first case. Concentrate the liquid, and crystals of Ammonium Bisulphate will be deposited:



To determine the Ratio of Nitrogen to Hydrogen in Ammonia. Perform the experiment described on page 251 (Fig. 82).

To determine the percentage of Ammonia in any Ammonium compound. (1) This determination depends for its working on the fact that when any Ammonium compound is boiled with a solution of Caustic Potash, Ammonia gas is driven off, and the alkaline properties of the Caustic Potash partly disappear.

This may be made clearer by the following example, in which Ammonium Chloride is used. The equation is:



56

17.

It is clear that the Caustic Potash, being changed into Potassium Chloride, loses its alkaline character, and is neutralized: also it appears from the equation that 56 grams of KOH will drive out 17 grams of Ammonia from any Ammonium salt. Consequently 1 c.c. of N. KOH solution, which contains .056 gram of KOH, will drive out .017 gram of Ammonia.

To perform the experiment, 1 gram of the Ammonium salt must be weighed out and placed in a flask; 50 c.c. of N. KOH are added, and the contents of the flask vigorously boiled, till the steam given off has no action on either red litmus or turmeric paper, shewing that all the Ammonia has been driven off.

N.B.—During the boiling the flask must be held in a slanting position to avoid loss by spurting.

When the boiling is finished, titrate the solution in the flask with N. H_2SO_4 , to find out how much of the 50 c.c. N. KOH is left unacted upon by the Ammonium salt.

It is clear that if the titration requires 20 c.c. of N. H_2SO_4 , 20 c.c. of the N. KOH must have been added in excess, and hence 30 c.c. has been used up. This contains enough KOH to liberate $30 \times .017$ grams of Ammonia, which must have been contained in the original gram of Ammonium salt: hence the percentage of Ammonia present in the salt can be readily calculated.

(2) Another method consists in taking 1 gram of the Ammonium salt, adding excess of strong KOH solution, and boiling off all the Ammonia. The Ammonia is led into a known volume of normal acid, part of which it neutralizes, and the quantity left unneutralized is determined by titration with N. KOH.

The apparatus used is shewn in the diagram (Fig. 90). One gram of the Ammonium salt is weighed out, and dissolved in about 25 c.c. of water: this is all placed in the flask, and half a stick of KOH is added. The delivery tube is fitted first with a bulb tube, to prevent any spurting over, and this is joined to a 50 c.c.

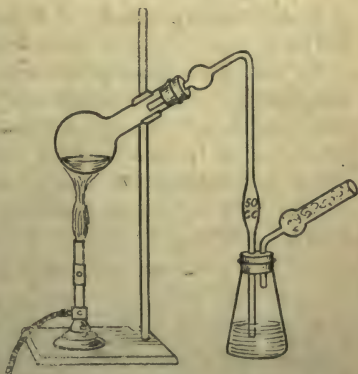


FIG. 90.

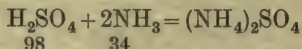
pipette, which passes through the cork of a flask containing 50 c.c. of the N. H_2SO_4 previously poured in through the drying tube, which is filled with broken pieces of glass.

Now boil the mixture in the flask (avoid bumping by putting in pieces of Platinum wire or a little clean sand); the Ammonia passes out through the pipette, which dips just below the surface of the N. H_2SO_4 , and, if any is not absorbed by the acid in the flask, it does not get past that left on the pieces of glass in the drying tube. "Sucking back" into the flask is prevented by the "bulge" of the pipette.

After boiling steadily for some time—say 10 minutes—disconnect the apparatus, wash the acid on the broken glass through into the flask with distilled water, and then titrate the acid with N. KOH , using litmus as an indicator.

Suppose 27 c.c. of N. KOH were required, indicating that 27 c.c. of the normal acid were still unneutralized, and that only 23 c.c. had been neutralized by the Ammonia.

Now every c.c. contains .049 gram of H_2SO_4 , and from the equation



it is clear that this weight of H_2SO_4 will neutralize .017 gram of Ammonia. Therefore the original salt must have contained $23 \times .017$ grams of Ammonia in 1 gram: hence the percentage is easily calculated.

To show the Oxidizing Action of Nitric Acid. (1) Take about 20 c.c. of strong Nitric Acid in a flask with a sufficiently wide mouth to allow the passage of a deflagrating spoon. Boil the Nitric acid till the flask is full of its vapour, and then introduce a *small* piece of lighted yellow Phosphorus in a deflagrating spoon. Note that the combustion increases in rapidity and brilliance, and that white fumes of Phosphorus Pentoxide and red fumes of Nitrogen Peroxide are liberated.

(2) Boil some flowers of Sulphur with concentrated Nitric acid for 10 minutes. Use a small flask, and perform the experiment in a fume cupboard. When action has ceased, filter the liquid and test the filtrate for Sulphuric acid by means of a solution of Barium Chloride.

(3) Warm some granulated Tin with strong Nitric acid in a boiling tube. When action has ceased, note the formation of a white precipitate. This consists of Hydrated Tin Oxide, $\text{SnO}_2 \cdot \text{H}_2\text{O}$.

(4) Warm some black Lead Sulphide, PbS , with strong Nitric acid. Note the formation of white Lead Sulphate, PbSO_4 .

To prepare a pure specimen of Nitric Oxide. Lead the gases evolved by the action of dilute Nitric acid on Copper through a solution of Ferrous Sulphate. Place the brown liquid thus obtained in a small flask fitted with a single delivery tube and warm gently. When all the air has been driven out of the flask, collect about half a boiling tube full of the gas over water.

To test its purity, allow Oxygen gas, from a cylinder, to bubble slowly into the test tube, shaking up the red fumes of Nitrogen Peroxide, which are formed, with water till they are dissolved, and then adding more Oxygen. The quantity of the gas gradually diminishes, and, if the gas was originally pure Nitric Oxide and the addition of Oxygen is made very cautiously, the whole of the gas in the test tube will disappear.

To prepare Liquid Nitrogen Peroxide. Perform the experiment described on page 266 (Fig. 89). The liquid Peroxide may be preserved by sealing up the ends of the U-tube with a blowpipe.

CHAPTER XXI.

ARGON AND THE OTHER INACTIVE GASES.

Discovery of Argon. The discovery of Argon in air is due to the combined efforts of Lord Rayleigh and Sir William Ramsay. In 1892-3 Lord Rayleigh was making a series of very accurate investigations on the densities of Oxygen, Nitrogen and Air. As was necessary for such careful experiments, the gases Oxygen and Nitrogen were made in various different methods in order to compare results.

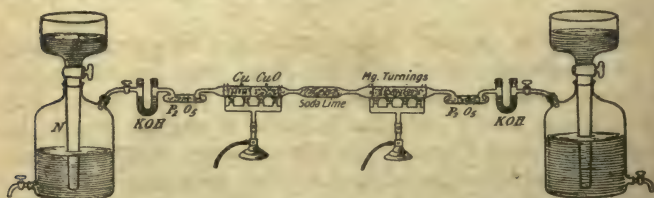


FIG. 91.—Separation of Nitrogen and Argon.

These results, as far as Oxygen was concerned, differed by about 1 part in 10,000, but with Nitrogen, he found that, when prepared from Ammonia, its density was .005 greater than that of Nitrogen obtained from Air, an error of 1 part in 200, and therefore difficult to account for.

Later, Sir William Ramsay conducted a series of experiments with atmospheric Nitrogen, passing it backwards and forwards over Magnesium turnings heated to redness. The apparatus was like that in the diagram (Fig. 91), various absorbents being used to render the gas thoroughly pure.

The first result (May, 1894) was to obtain a gas with a density 15 times as great as that of Hydrogen. Next, the process of separation was carried on for ten days and further increase in density was noticed, till finally a gas was obtained which did not diminish at all in volume when passed over the red-hot Magnesium, and its density was found to be 19.086. This remaining gas was mainly Argon.

Later, the combined experimenters, Rayleigh and Ramsay, invented an apparatus by which the Argon was obtained from Air much more quickly. Air and Oxygen, in proper proportion, are subjected to a fan-shaped electric discharge, and the Oxides of Nitrogen formed are dissolved at once by a spray of Caustic Soda solution injected into the vessel; by this means fairly pure Argon can be obtained in a few hours. The results of their labours was to prove that Atmospheric Nitrogen contained 1.186 per cent. of Argon.

Argon has also been found in a few rare minerals and in mineral springs, but no trace of it can be discovered in any animal or vegetable matter, however rich they may be in Nitrogen.

Properties of Argon. Argon resembles Nitrogen in most of its properties, but it is much more inert than Nitrogen. It forms no known compound with any other element, and the failure of many attempts to make it combine led to the choice of its name Argon, or the idle element. Even a mixture of Argon and Fluorine when subjected to a rain of electric sparks shewed no signs of combination.

The latest determination of the density of Argon is 19.96, and this is therefore the Equivalent Weight, but, owing to the fact that it forms no compounds, its Atomic Weight is very difficult to determine. By a method of reasoning, which is too complicated to be noted here, the conclusion has been arrived at that the molecule of Argon contains only one atom. Allowing this, its Atomic Weight must be double its Vapour Density, namely, 39.92.

OTHER GASES IN AIR.

Helium. In 1868, during an eclipse of the sun, the spectro-scope was first employed to examine the atmosphere round the sun, and certain lines were noted which were distinct from those of any element known at that time. To this unknown element, which produced these lines, the name of Helium was given. Thirty years later, Ramsay discovered the presence of this gas in a rare mineral called Cleveite, and since then its presence has been detected in many mineral waters, notably those of Bath, and also in Air.

Like Argon, Helium is a colourless, odourless gas, and has no known compound; also its molecule is monatomic, and, as its density is 2 (it is the next lightest element to Hydrogen), its Atomic Weight is taken as 4.

The spectrum of Helium is a very brilliant one and has, amongst others, a bright line in the yellow, very near to the Sodium lines, for which element it was at first mistaken.

Krypton, Neon and Xenon. By the careful fractional distillation of liquid air, three other gases, to which the names Krypton, Neon and Xenon were given, have been isolated. They all of them resemble Argon in their properties. No compounds are known, and their molecules are monatomic.

They only occur in infinitesimal quantities in the air, as is seen in the following table :

Argon	-	-	-	1 part in 107 of air.
Neon	-	-	-	1 „ 80,800 of air.
Helium	-	-	-	1 „ 245,300 of air.
Krypton	-	-	-	1 „ 20 millions of air.
Xenon	-	-	-	1 „ 170 millions of air.

Their Atomic Weights have been determined, and are as follows : Neon 20, Krypton 82 and Xenon 128.

These inactive elements, Helium, Neon, Argon, Krypton and Xenon fall naturally into one group in Mendeleeff's table of the elements (p. 137), part of which is repeated

here to shew their relation to one another and to other elements :

Hydrogen. 1.	Helium. 4.	Lithium. 7.	Berythium. 9.
Fluorine. 19.	Neon. 20.	Sodium. 23.	Magnesium. 24.
Chlorine. 35.5.	Argon. 40.	Potassium. 39.	Calcium. 40.
Bromine. 80.	Krypton. 82.	Rubidium. 85.	Strontium. 87.
Iodine. 127.	Xenon. 128.	Caesium. 133.	Barium. 137.

CHAPTER XXII.

PHOSPHORUS AND ITS COMPOUNDS.

PHOSPHORUS.

Symbol, P. Atomic Weight, 31. Molecular Weight, 124.

History. Phosphorus was first made by Brand of Hamburg (1669), who obtained it by distilling a mixture of sand and urine which had been evaporated to a thick syrup. Robert Boyle (1680) also made some Phosphorus, but it was considered a chemical curiosity till Scheele (1771) introduced the method for obtaining it from bone ash.

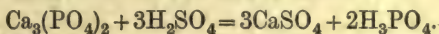
Occurrence. Phosphorus is found in very few minerals, the one occurring most commonly being a combined Phosphate and Chloride of Calcium called *Apatite*, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$. It is, however, disseminated as Phosphates in small quantities in most soils, and is essential to the growth of many plants.

The chief source of Phosphorus is bones, which contain about 60 per cent. of Calcium Phosphate, $\text{Ca}_3(\text{PO}_4)_2$. Many substances may be extracted from bones by using various solvents such as Alcohol, Benzene, Ether, etc.; the residue yields glue when digested with water under pressure, and when this is taken away, Animal Charcoal can be obtained from the remainder by distilling away the bone oil. The Calcium Phosphate is still contained in the Animal Charcoal, and may be obtained from it, or from bones directly, by burning them in an open fire, the "bone ash" consisting mainly of this compound.

Manufacture. Two methods are still in use for extracting the Phosphorus from bone ash. The older or retort process

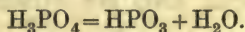
is now dying out and being replaced by the more modern electrical process.

In the retort process, the bone ash is first mixed with the proper quantity of Sulphuric acid to change it into Calcium Sulphate and liberate Orthophosphoric acid :



↓

The Orthophosphoric acid is filtered away from the precipitated Calcium Sulphate and heated till it is of a syrupy consistency ; it is then Metaphosphoric acid :



The syrup is then mixed with about one-fourth of its weight of Coke or Charcoal and heated to redness in fireclay retorts

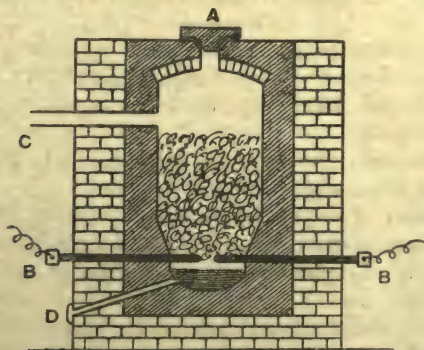
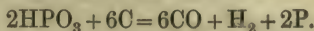


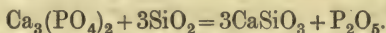
FIG. 92.—Electrical Furnace for the manufacture of Phosphorus.

which have their necks dipping under water. Hydrogen, Carbon Monoxide and Phosphorus vapour are evolved, and the last-named condenses in the water :

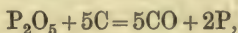


The electrical process consists in mixing the bone ash with finely divided Silica and Coke and subjecting the mixture to the very high temperature of the electric arc. The apparatus is shewn diagrammatically in Fig. 92. The mixture is fed in

through *A* and heated by passing a strong alternating current between the two Carbon poles *BB*. At the high temperature produced Calcium Silicate and Phosphorus Pentoxide are first formed :



The Phosphorus Pentoxide is reduced by the Carbon :



and the mixture of Carbon Monoxide and Phosphorus vapour is led away, through the flue *C*, into water, where the Phosphorus is condensed. The Calcium Silicate becomes molten, and is got rid of, through *D*, by tapping the furnace from time to time.

The crude Phosphorus thus obtained contains Carbon and other impurities, but the methods of purification are guarded as trade secrets. It has been stated that it is purified by distillation and also by filtering the molten Phosphorus through chamois leather. Ultimately it is put on the market in the form of sticks.

Properties. Freshly prepared Phosphorus is a translucent, almost colourless, wax-like solid. After a time, even if kept in the dark, it loses its transparency, and becomes coated with an opaque, white film, while, if exposed to light, it darkens almost at once, becoming first yellow then brown, and finally almost black.

At 0° C. Phosphorus becomes brittle and has a crystalline fracture, but, at ordinary temperatures, it is soft enough to be cut with a knife. Its density is 1.8. It melts, under water, at a temperature of 44° C., and boils at 290° C.

Phosphorus volatilizes at ordinary temperatures, and if a small quantity is placed in a sealed vacuous tube and kept for some days in the dark, brilliant colourless crystals are formed on the sides of the tube.

Phosphorus ignites at a temperature of about 30° C. in moist air, but, the drier the air, the higher the ignition point, and, as has already been seen (p. 29), Phosphorus may actually be distilled in perfectly dry Oxygen without igniting.

On account of this low temperature of ignition, Phosphorus is always kept under water, and should never be handled with the bare fingers except under water. Burns caused by Phosphorus are very painful and heal slowly. Persons exposed for any length of time to the fumes of Phosphorus, those, for instance, employed in the manufacture of matches at one time, are liable to suffer from rotting of the bones of the jaw and nose, a disease called "phossy jaw."

When Phosphorus is exposed to moist air at ordinary temperatures, it becomes faintly luminous, owing to slow combustion and oxidation. White fumes with an unpleasant garlic smell are evolved, and these consist mainly of the lower Oxide of Phosphorus, P_4O_6 . This glowing in air does not take place below $0^\circ C.$, and, in pure Oxygen, no phosphorescence is seen below $15^\circ C.$; it is believed to be due to the presence of minute quantities of Ozone in air, as it stops immediately a little Turpentine, which dissolves Ozone, is introduced into the jar.

When water, which has beneath it a small quantity of Phosphorus, is distilled in the dark, a luminous ring is seen at the point in the condenser where the water condenses, and Phosphorus globules collect in the receiver. This forms a very delicate test for the presence of free Phosphorus.

Phosphorus is practically insoluble in water—1 part in 300,000—but it dissolves readily in Carbon Disulphide, Chloroform, Benzene, Turpentine and similar solvents.

If a few drops of a solution of Phosphorus in Carbon Disulphide are placed on a piece of filter paper and then allowed to evaporate in air, when all the solvent has gone, a thin layer of Phosphorus is left on the paper, which ignites spontaneously owing to the heat evolved during oxidation being sufficient to raise a portion of the Phosphorus up to ignition temperature.

Whenever Phosphorus burns, either in air or Oxygen, the white fumes evolved consist of Phosphorus Pentoxide, P_2O_5 .

RED PHOSPHORUS.

Besides ordinary Phosphorus, another allotropic variety is known. This exists as a red amorphous powder, and is usually called Red Phosphorus to distinguish it from the ordinary kind, which is called Yellow Phosphorus.

The red form is prepared by carefully heating Yellow Phosphorus, out of contact with air, to a temperature of 240° to 250° C. The change will take place at 200° C. if a little Iodine is mixed with the Phosphorus.

Red Phosphorus is manufactured nowadays in large quantities by heating the ordinary variety in a cast-iron pot, regulating the temperature with extreme care by accurate thermometers encased in iron jackets, as the molten Phosphorus attacks glass. Care is needed because, if the temperature rises to 260° , the Red Phosphorus changes back into the ordinary modification with the evolution of considerable heat, and the pot is liable to burst.

Properties. Red Phosphorus is a chocolate-red powder, having a density of 2.12. Its properties are very different from those of the yellow variety; it does not phosphoresce, it has no smell and is non-poisonous.

It is not soluble in water or Carbon Disulphide or any of the substances which will dissolve the yellow kind.

It does not ignite till a temperature of 260° is reached, and probably changes into Yellow Phosphorus before ignition.

Red Phosphorus only burns in Chlorine when heated, whilst Yellow Phosphorus is spontaneously inflammable in this gas.

Equal weights of Red and Yellow Phosphorus produce equal weights of Phosphorus Pentoxide when burnt, proving that each contains nothing but the element. The difference in properties is probably due either to a difference in the arrangement of the molecules or to a difference in the number of atoms in each molecule.

The properties of the two varieties are compared in the following table :

Property.	Red Phosphorus.	Yellow Phosphorus.
Colour - - -	Chocolate red.	Almost colourless.
Smell, etc. - - -	Odourless, tasteless.	Garlic smell.
In moist air - - -	No phosphorescence or oxidation.	Phosphorescence and oxidation.
Melting point - - -	Above 500° C.	44° C.
Physiological action -	Non-poisonous.	Poisonous.
Density - - -	2.12	1.84.
Action of CS ₂ - - -	Insoluble.	Soluble.
Temperature of ignition - - -	260°.	30°.
Electric current - - -	Feeble conductor.	Non-conductor.
With Chlorine - - -	Ignites if heated.	Ignites spontaneously.

Atomic and Molecular Weights of Phosphorus. The combining weight of Phosphorus, as determined by the analysis of Silver Phosphate, is found to be 31, and as no smaller weight has been found in the molecule of any of its volatile compounds—such as PH₃ or PCl₃—this weight is taken as the Atomic Weight of the element.

The Density of Phosphorus vapour, according to Mitscherlich, is 64.5 at 1000° C. Hence its molecular weight is 129, and it must contain four atoms in its molecule. Above 1500° the density of the vapour begins to decrease, shewing that dissociation is taking place, and that the P₄ molecules are becoming P₂.

The value of the molecular weight found by the depression of the freezing point of Carbon Disulphide also corresponds to a 4-atom molecule.

Matches. The head of a match which will ignite by friction used to contain yellow Phosphorus, Manganese Dioxide and glue with some colouring matter. The heat generated by the friction starts the Phosphorus burning, and the Manganese Dioxide (Saltpetre is sometimes substituted for this substance) aids the combustion of the wood or wax of which the stick is made.

Nowadays, owing to the danger to the health of the

workers, red Phosphorus is substituted for yellow in most match factories. The red Phosphorus is mixed in a paste with powdered glass and glue, and a strip is put on the sides of the boxes and used for rubbing the "head" of the match to start combustion. The "heads" consist of a mixture of Antimony Sulphide, Potassium Chlorate and glue. They are called safety matches, because they will not ignite by friction on a rough surface, but they can be ignited by rubbing them quickly along a smooth non-conducting surface such as glass.

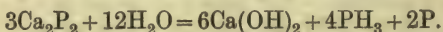
COMPOUNDS OF PHOSPHORUS AND HYDROGEN.

Three compounds of Phosphorus and Hydrogen are known : PH_3 (gas), P_4H_2 (liquid), $(\text{P}_4\text{H}_2)_3$ (solid). Only the first-named is of much importance.

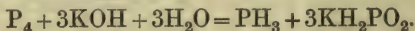
PHOSPHORETTED HYDROGEN. PHOSPHINE.

Formula, PH_3 . Molecular Weight, 34.

Preparation. Phosphine is formed in small quantities when red Phosphorus is gently heated in a stream of Hydrogen gas. This clearly indicates its composition. It is also evolved by the action of water upon Calcium Phosphide :



The best way of preparing this gas in the laboratory is by boiling some yellow Phosphorus in a flask with a strong solution of Caustic Potash :



The substance left in the flask is Potassium Hypophosphite.

Owing to the fact that a small amount of liquid Hydrogen Phosphide, P_4H_2 , is always evolved at the same time, the gas is spontaneously inflammable in air, so, for safety's sake, the flask may be filled with coal gas before commencing to heat the mixture (see Fig. 93). When the bubbles of Phosphine burst after rising to the surface of the water, they ignite with

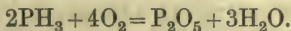
a slight explosion and a flash of light, forming vortex rings of Phosphorus Pentoxide when the air is still.

If the gas is passed through a freezing mixture, which condenses the liquid P_4H_2 , the Phosphine is no longer spontaneously inflammable.

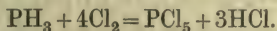


FIG. 93.—Preparation of Phosphine.

Properties. Phosphine is a colourless gas with an odour like decaying fish. Fish that have been dead for some time are luminous in the dark, possibly because they evolve this gas in small quantities. The pure gas ignites at a temperature of 100° C. in air or Oxygen, forming Phosphorus Pentoxide and water:



When a jet of Phosphine is placed in Chlorine gas, it ignites spontaneously, forming Phosphorus Pentachloride and Hydrochloric acid gas:



It is a highly poisonous gas and very little can be breathed with impunity.

Phosphine is only slightly soluble in water and its solution has no effect upon litmus or turmeric paper; in this it does not resemble its Nitrogen analogue, Ammonia gas, but it does resemble it in combining with Hydrochloric, Hydrobromic and Hydriodic acids, forming Phosphonium salts. These

unions do not take place so readily as the corresponding reactions with Ammonia, but the mixed gases will unite when passed through a tube surrounded by a freezing mixture.

The three salts formed are called Phosphonium Chloride PH_4Cl , Phosphonium Bromide, PH_4Br , and Phosphonium Iodide, PH_4I . They are all white crystalline salts which sublime, when heated, in a similar manner to the corresponding Ammonium salts.

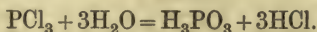
CHLORIDES OF PHOSPHORUS.

Phosphorus forms two very important compounds with Chlorine: Phosphorus Trichloride, PCl_3 , and Phosphorus Pentachloride, PCl_5 .

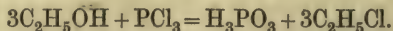
Phosphorus Trichloride PCl_3 . This substance is formed by passing dry Chlorine gas over red Phosphorus gently warmed in a retort. The Trichloride may be collected in a well cooled receiver.

It is a colourless mobile liquid with a pungent smell. It boils at 74°C ., and fumes in moist air.

It combines with water, forming a mixture of Phosphorous and Hydrochloric acids:



A similar reaction occurs when this substance is mixed with any compound containing the Hydroxyl (OH) radicle. Thus, with Alcohol:

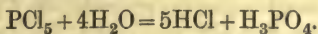


Its vapour density according to Dumas is 70 ($\text{H}=1$), and this agrees quite well with a formula of PCl_3 , which would have a theoretical vapour density of 68.75.

Phosphorus Pentachloride PCl_5 . This compound is formed when Phosphorus burns in a jar of Chlorine gas. It may best be prepared by allowing the Trichloride to fall drop by drop into a jar of Chlorine gas (Fig. 94).

Properties. Phosphorus Pentachloride is a yellowish white solid, with an irritating smell. It is very poisonous.

It fumes when it comes into contact with moist air, combining with the water to form Hydrochloric and Phosphoric acids :



It sublimes readily, when heated, at a temperature below 100°C. , and as its vapour is heated it dissociates more and more completely into a mixture of Phosphorus Trichloride and free Chlorine. This change is seen by the change in colour, as the vapour, colourless at first, shews more and more the yellowish green colour of Chlorine, but the dissociation is best proved by determinations of the vapour density.



FIG. 94.—Preparation of Phosphorus Pentachloride.

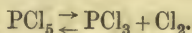
For a formula PCl_5 the density ($\text{H} = 1$) should be

$$\frac{204.25}{2} = 102.125.$$

The density of Phosphorus Pentachloride is never quite as high as that, even at low temperatures, and it becomes gradually less as the temperature rises, being 69.2 at 200°C. and 52.06 at 300°C. , above which temperature it remains constant. This density, it will be noted, is exactly half the calculated density of PCl_5 ; this is because one molecule of PCl_5 has dissociated into two molecules of $\text{PCl}_3 + \text{Cl}_2$. The same quantity of matter occupies double the space, and its density is therefore one-half.

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The action is reversible, as the Trichloride of Phosphorus and Chlorine reunite on cooling :



Phosphorus forms very similar compounds to its Chlorides with Bromine and Fluorine, except that in the latter case the Pentafluoride is a stable compound and does not dissociate on heating, indicating, in this compound at any rate, the penta-valency of Phosphorus. In most of its compounds, as has probably been already noticed, Phosphorus is tri-valent.

OXIDES OF PHOSPHORUS.

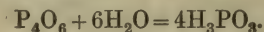
Three compounds of Phosphorus and Oxygen are known, and they are all produced when Phosphorus is burnt in a limited supply of air :

Phosphorous Oxide, Phosphorus Trioxide	-	P_4O_6 .
Phosphorus Tetroxide	- - - -	P_2O_4 .
Phosphoric Oxide, Phosphorus Pentoxide	-	P_2O_5 .

Only the first and last-named Oxides are of sufficient importance to be considered in detail.

Phosphorous Oxide P_4O_6 . When Phosphorus is burnt in a slow current of air, a mixture of this substance and Phosphorus Pentoxide is formed. If the products of combustion are led through a condenser tube surrounded by water at 60°C ., and containing glass wool, the Pentoxide is stopped by the wool and only the Phosphorous Oxide gets through, and may be condensed in a tube surrounded by a freezing mixture.

Properties. Phosphorous Oxide is a white crystalline solid which has an unpleasant garlic smell and is highly poisonous. When exposed to air it slowly oxidizes to the Pentoxide, P_2O_5 , and, when placed in warm Oxygen, it bursts into flame, forming the same compound. It slowly dissolves in cold water, forming Phosphorous acid :



Its vapour density is 110 ($H=1$). This corresponds to a formula P_4O_6 , though the simpler formula P_2O_3 is often used for this substance.

Phosphorus Pentoxide P_2O_5 . When Phosphorus is burnt in excess of air or Oxygen, the chief product of combustion is Phosphorus Pentoxide. If the combustion takes place in a crucible placed on a glass plate (Fig. 95) and covered by a large bell-jar, the white fumes of the Pentoxide fall like snow-flakes and collect on the glass plate, from which they may be scraped up and kept in a well-stoppered bottle.

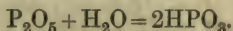


FIG. 95.—Preparation of Phosphorus Pentoxide.

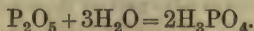
Properties. Phosphorus Pentoxide is a light, white, amorphous powder, which has no smell. The garlic smell, usually possessed by this substance, is due to impurities of Phosphorous Oxide, etc.

Phosphorus Pentoxide sublimes slowly when warmed, and rapidly at a temperature of $250^{\circ}C$. Its vapour density at temperatures over 1000° is about 145. This corresponds to the molecular weight of 290 and a formula P_4O_{10} , but the simpler formula P_2O_5 is generally employed for the sake of convenience.

Phosphorus Pentoxide is extremely hygroscopic, a little of the solid left exposed to air for a few minutes becomes quite liquid. When mixed with water, combination takes place with a hissing sound like the quenching of red-hot Iron. This is due to the large amount of heat evolved. If the water is cold, Metaphosphoric acid is formed :

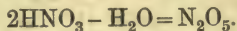


But if P_2O_5 is thrown into boiling water, Orthophosphoric acid is formed :

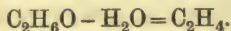


On account of its great affinity for water, Phosphorus Pentoxide is used for drying gases. This substance will also

take the elements of water from many compounds which contain them. Thus, with Nitric acid, Nitrogen Pentoxide is left :



Similarly with Alcohol, Ethylene remains :

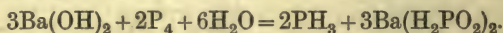


OXY-ACIDS OF PHOSPHORUS.

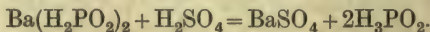
Phosphorus forms five Oxy-acids, all of which are of considerable importance :

Name.	Formula.	Corresponding Oxide.
Hypophosphorous acid	H_3PO_2 or $\text{POH}_2(\text{OH})$	- Not known.
Phosphorous acid	H_3PO_3 or $\text{POH}(\text{OH})_2$	P_4O_6 .
Orthophosphoric acid	H_3PO_4 or $\text{PO}(\text{OH})_3$	P_2O_5 .
Pyrophosphoric acid	$\text{H}_4\text{P}_2\text{O}_7$	P_2O_5 .
Metaphosphoric acid	HPO_3 or $\text{PO}_2(\text{OH})$	P_2O_5 .

Hypophosphorous Acid H_3PO_2 . When yellow Phosphorus is boiled with Barium Hydroxide, a similar reaction takes place to that which occurs with Caustic Potash, and Barium Hypophosphite is formed :

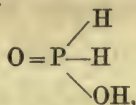


If the solution thus obtained is treated with dilute Sulphuric acid, a white precipitate of Barium Sulphate is thrown down and Hypophosphorus acid remains in solution, and can be obtained by filtering from the precipitate and gently evaporating the solution :



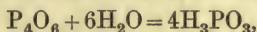
Properties. Hypophosphorous acid occurs as white crystals which dissolve readily in water. The solution is a feeble mono-basic acid, as only one of the three Hydrogen atoms is replaceable by metals. The salts are called Hypophosphites.

Its structural formula may be written :

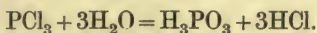


and it is the Hydrogen atom in the Hydroxyl which is replaceable.

Phosphorous Acid H_3PO_3 . This acid is formed by the solution of Phosphorous Oxide, P_4O_6 , in cold water :



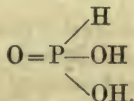
or, better, by the action of Phosphorus Trichloride on water :



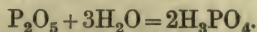
When either of these solutions is evaporated, till the temperature has reached 180°C. , and then allowed to cool, the Phosphorous acid separates out as white crystals.

Phosphorous acid is a powerful reducing agent, owing to the fact that it is quite ready to take up another atom of Oxygen and become Orthophosphoric acid, H_3PO_4 . It reduces Silver Nitrate to Silver, Gold Chloride to Gold and Copper Sulphate to Copper.

Phosphorous acid usually behaves as a di-basic acid, only two of its Hydrogen atoms being replaceable by metals. Its structural formula may therefore be written :



Orthophosphoric Acid H_3PO_4 . This acid is formed when Phosphorus Pentoxide is added to boiling water or when a solution of this substance in cold water is boiled :



It is also obtained by boiling Phosphorus with Nitric acid for some time, using a reflex condenser (Fig. 96), so that the vapours of Nitric acid are returned to the flask.

By concentrating the solution till its boiling point is 140°C . and then allowing it to cool, the Phosphoric acid separates out as transparent rhombic crystals.

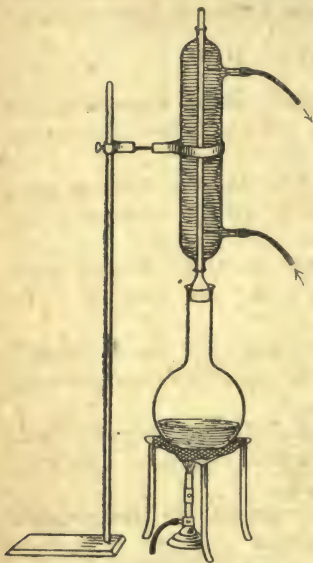


FIG. 96.—Preparation of Phosphoric acid.

Phosphoric acid is a tri-basic acid, all three of its Hydrogen atoms being replaceable by metals. It therefore forms three salts with the metal Sodium:

Sodium Di-Hydrogen Phosphate
 NaH_2PO_4 .

Di-Sodium Hydrogen Phosphate
 Na_2HPO_4 .

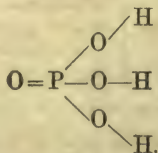
Sodium Phosphate Na_3PO_4 —
the Normal Salt.

Of these the Di-Sodium salt is neutral to litmus, the Mono-Sodium salt is acid and the Normal salt is Alkaline to litmus.

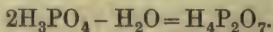
The three Hydrogen atoms may be replaced by different elements, and a good example of this is seen in Microcosmic

Salt, Ammonium Sodium Hydrogen Phosphate, $\text{NH}_4\cdot\text{Na}\cdot\text{HPO}_4$.

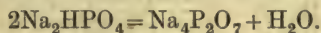
The constitution of the acid is seen in the formula:



Pyrophosphoric Acid $\text{H}_4\text{P}_2\text{O}_7$. This acid is formed when Orthophosphoric acid is heated to 220°C . One molecule of Water is driven off from two molecules of the acid:



The acid is tetra-basic and its salts are called Pyrophosphates. Sodium Pyrophosphate is formed when the Di-Sodium Orthophosphate (called Sodium Phosphate by the chemist) is heated strongly :



By boiling the acid itself (or any soluble Pyrophosphate) with dilute Sulphuric acid, it is converted into Orthophosphoric acid (or an Orthophosphate).

Metaphosphoric Acid HPO_3 . This acid is formed when Phosphorus Pentoxide is allowed to deliquesce in moist air or when Orthophosphoric acid is heated to redness.

Metaphosphoric acid is a transparent, vitreous solid, sometimes called "glacial Phosphoric acid." It fuses at 0°C ., and is usually cast into sticks.

Metaphosphoric acid is a mono-basic acid, but it forms a curious series of salts, which may be regarded as being derived from polymeric* varieties of the acid.

Thus Sodium Metaphosphate is NaPO_3 , Potassium Di-Metaphosphate, $\text{K}_2\text{P}_2\text{O}_6$, Sodium Tri-Metaphosphate, $\text{Na}_3\text{P}_3\text{O}_9$, Lead Tetra-Metaphosphate, $\text{Pb}_2\text{P}_4\text{O}_{12}$.

The ortho-, pyro- and metaphosphates are distinguished from one another by the following tests :

Test.	Orthophosphate.	Pyrophosphate.	Metaphosphate.
Silver Nitrate.	Yellow precipitate.	White crystalline precipitate.	White gelatinous precipitate.
Barium Nitrate.	No precipitate unless alkaline.	No precipitate unless alkaline.	White precipitate.
Albumen.	No action.	No action.	Coagulates.

All the Phosphoric acids give a yellow precipitate with a large excess of a hot solution of Ammonium Molybdate in Nitric acid.

* Substances are said to be "polymeric" which have the same percentage composition, but whose molecular weights are multiples of one another; e.g. Acetylene, C_2H_2 , and Benzene, C_6H_6 .

PROBLEM.

58. 40 grams of Phosphorus Pentachloride is boiled with excess of water. What volume of gas is evolved at 210° C. and 760 mm. pressure ?
(Camb. Univ. Schol. Exam.)

PRACTICAL EXERCISES.

To prepare Phosphine. Use the apparatus shewn in Fig. 93. Place in it a *strong* solution of Caustic Potash and a piece of yellow Phosphorus not bigger than a pea. Pass coal gas through the apparatus till the air is all driven out, then stop the flow of gas and heat till the liquid boils.

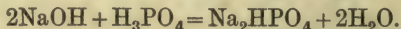
To prepare Phosphorus Pentoxide, Metaphosphoric and Orthophosphoric Acids. Burn some yellow Phosphorus in a crucible under a bell-jar placed on a glass plate (Fig. 95). When combustion ceases and the fumes have condensed, admit more air and combustion will commence again.

Dissolve the white Pentoxide of Phosphorus produced in distilled water; the acid produced is Metaphosphoric acid.

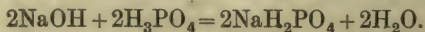
Boil half the solution thus obtained for fully 10 minutes; it will change into Orthophosphoric acid.

Apply to these solutions the tests for Ortho- and Metaphosphoric acids given on page 293.

To prepare the three Orthophosphates of Sodium. Make a dilute solution of Orthophosphoric acid as described above, and place it in a burette. Take 25 c.c. of a dilute solution of Caustic Soda in a beaker and titrate it with the acid solution till it is neutral. Concentrate the liquid thus obtained, and allow it to crystallize. The crystals are those of Di-Sodium Mono-Hydrogen Orthophosphate, Na_2HPO_4 :



Now take another 25 c.c. of the same Caustic Soda solution and add to it exactly twice the amount of the Orthophosphoric acid. Concentrate and crystallize. These crystals are those of Mono-Sodium Di-Hydrogen Orthophosphate, NaH_2PO_4 :

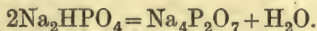


To obtain crystals of the Normal Phosphate Na_3PO_4 , use 37.5 c.c. of the same Caustic Soda solution ($1\frac{1}{2}$ times as much as in the other cases), and add the same quantity of Orthophosphoric acid as was needed to neutralize 25 c.c. of Caustic Soda :



Examine the three sets of crystals under a microscope, and notice difference in shape, etc.

To prepare Sodium Pyrophosphate. The common Phosphate of Soda has a formula Na_2HPO_4 . Powder some crystals of it and fill about 1 inch of an ordinary test tube with the powder. Heat strongly, inclining the tube so as to allow the water evolved to drip away. The white solid left is Sodium Pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$:



Dissolve some of this salt in distilled water and apply the tests for Pyrophosphoric acid given on page 293.

CHAPTER XXIII.

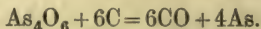
ARSENIC, ANTIMONY AND BISMUTH.

ARSENIC.

Symbol, As. Atomic Weight, 75. Molecular Weight, 300.

Occurrence. Arsenic occurs to a small extent free in nature, and combined in a large number of minerals: Sulphides—*Realgar*, As_2S_2 ; *Orpiment*, As_2S_3 ; *Mispickel* or Arsenical Pyrites, FeAsS : Arsenides—*Arsenical Iron*, FeAs_2 and Fe_4As_3 and *Kupfernickel*, NiAs . Arsenic is also almost always present in Iron Pyrites, FeS_2 , hence it finds its way into Sulphuric acid, which is made from Pyrites, and into the atmosphere of towns, because of the Pyrites which is often present in coal.

Preparation. On a small scale Arsenic can be made by heating a mixture of Arsenic Oxide, White Arsenic, As_4O_6 , with powdered Charcoal in a crucible and subliming the Arsenic evolved in a conical metal cup which fits over the top of the crucible:



Properties. Ordinary Arsenic is a steel-grey metallic-looking substance, highly crystalline, and, on that account, very brittle. It is a good conductor of heat and electricity. Its density is 5.7, which is higher than that of typical non-metals. In its physical properties, therefore, Arsenic is seen to resemble mostly the metals, but chemically, as will be seen later, its affinities are with the non-metals. It is usually called a *Metalloid*.

When heated, it begins to vaporize slowly, without melting, at 100°C ., and much more rapidly at a red heat. The vapour has a yellow colour and a garlic smell. By condensation of the vapour in different ways two allotropic modifications of grey Arsenic—yellow and black Arsenic—have been isolated.

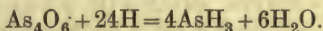
Arsenic burns in Oxygen with a bluish flame, forming Arsenious Oxide, As_4O_6 .

It is insoluble in water, and is changed by Nitric and Sulphuric acids into its Oxide, As_4O_6 . In Chlorine, Arsenic inflames spontaneously, forming Arsenic Trichloride, AsCl_3 .

Arsenic is capable of forming alloys with metals, and a little of this element alloyed with Lead is used for making Lead shot, its effect being to make the drops of molten Lead, falling in the shot tower, more spherical and the resultant shot harder.

The density of Arsenic vapour is 150 ($\text{H}=1$). This indicates a Molecular Weight of 300 and a molecule containing four atoms— As_4 .

Arseniuretted Hydrogen, Arsine AsH_3 . This gas is formed when any soluble Arsenic compound is reduced with nascent Hydrogen (see Marsh's test for Arsenic, p. 300). With Arsenious Oxide, the equation is



Properties. Arseniuretted Hydrogen is a colourless gas, with an offensive smell. It is highly poisonous.

It is slightly soluble in water.

The gas burns with a lilac-coloured flame, forming Water and white fumes of As_4O_6 :



Arseniuretted Hydrogen is readily decomposed by heat into its elements, and, if a glass tube conveying the gas is heated by a bunsen burner, a black deposit of Arsenic is formed in the cold part of the tube beyond the flame.

When passed into a solution of Silver Nitrate, this gas acts as a reducing agent, and a black precipitate of metallic Silver is thrown down:



Arsenic and the Halogens. Arsenic forms similar compounds with all four members of the Halogen group, each compound containing three atoms of the Halogen and one atom of Arsenic, *e.g.* AsCl_3 , AsF_3 , etc. They are all made by the direct union of Arsenic and the Halogen, and are colourless fuming liquids at ordinary temperatures. They are all very poisonous.

OXIDES OF ARSENIC.

Arsenic forms two compounds with Oxygen, Arsenious Oxide, As_2O_3 , and Arsenic Oxide (Arsenic Pentoxide), As_2O_5 .

Arsenious Oxide As_2O_3 . This compound is the most important compound of Arsenic, and, in commerce, is often called "White Arsenic" or simply "Arsenic." It is formed where Arsenic itself is oxidized either by burning in a stream of air or by Nitric acid.

Properties. Arsenious Oxide can be obtained in three different forms: (1) Amorphous, (2) Octohedral crystals, (3) Rhombic crystals. They are produced when the vapour of the Oxide sublimes under different conditions as to temperature. The stable variety is the Octohedral crystal-line form, and the other two varieties gradually pass into it in time.

Arsenious Oxide dissolves sparingly in water and its solution is feebly acid, this action being probably due to the formation of unstable Arsenious acid, H_3AsO_3 . This acid has never been isolated, and, if the solution is concentrated, crystals of Arsenious Oxide separate out.

The vapour density of Arsenious Oxide, up to between 500°C . and 800°C ., corresponds to the formula As_4O_6 , but at 1700° its density decreases by one half, and therefore corresponds to the formula As_2O_3 .

Arsenious Oxide is a deadly poison, a dose of 6 milligrams is a fatal one for a man, but it is possible to accustom the system to much larger doses by the habitual use of it. It is said to improve the wind and beautify the complexion.

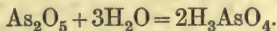
The antidote, in cases of Arsenic poisoning, is freshly

precipitated Ferric Hydrate, made by adding Ammonium Hydrate to Ferric Chloride.

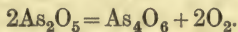
Arsenious Oxide is used in the making of paints, particularly green colours. As these pigments are often used in wallpapers, there is danger attending such papers.

Arsenic Pentoxide As_2O_5 . This Oxide is not formed like the corresponding Pentoxide of Phosphorus, when Arsenic is burnt in Oxygen. When Arsenious Oxide is heated with Nitric acid, Arsenic acid, H_3AsO_4 , is formed, and this yields Arsenic Pentoxide when strongly heated.

Properties. It is a white deliquescent solid, dissolving readily in water, forming Arsenic acid, H_3AsO_4 :



When heated to a bright-red heat, Arsenic Pentoxide, unlike Phosphorus Pentoxide, splits up, yielding Arsenious Oxide and Oxygen:



OXY-ACIDS OF ARSENIC.

The Oxy-acids of Arsenic correspond to some extent with those of Phosphorus. The acid corresponding to Phosphorous acid, H_3PO_3 , is not known except, possibly, in dilute solution, but salts derived from it are well known and are called Arsenites.

Three Arsenic acids, corresponding to the three Phosphoric acids, are known: Orthoarsenic, H_3AsO_4 , Pyroarsenic, $\text{H}_4\text{As}_2\text{O}_7$, and Metarsenic, HAsO_3 .

Their salts are called Arsenates, with the proper prefix according to the acid from which they are derived, and they are isomorphous with the corresponding Phosphates.

ARSENIC AND SULPHUR.

Arsenic forms three compounds with Sulphur:

Orpiment As_2S_3 , a bright yellow powder, found as a mineral and used as paint; hence its name from the Latin *auri pigmentum*. This compound is thrown down as a precipitate

when Sulphuretted Hydrogen is passed through a solution of an Arsenious salt and Hydrochloric acid.

Realgar As_2S_2 , a red brittle solid found as a mineral and used in fireworks, as it burns in air with a bright blue flame.

Arsenic Pentasulphide As_2S_5 , found as a pale yellow precipitate when Sulphuretted Hydrogen is rapidly passed through a solution of Arsenic acid in Hydrochloric acid.

Tests for Arsenic. It is most important, for criminal purposes, to have reliable and delicate tests for the presence of Arsenic. Two of those most generally used are appended.

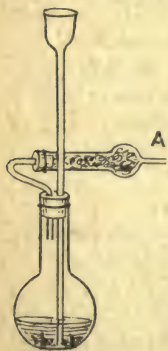


FIG. 97.—Marsh's test for Arsenic.

(1) *Marsh's Test.* Hydrogen is made in a small flask (Fig. 97) from pure Zinc and pure Hydrochloric acid. It is dried by being passed through a Calcium Chloride tube, and, when all the air has been driven out of the flask, a light is applied at *A* and a jet of burning Hydrogen is formed. This is tested first by allowing it to impinge on a piece of cold porcelain, such as a crucible lid, when it should deposit nothing but water. If a few drops of the solution of any soluble Arsenic compound are added through the funnel, the action in the flask becomes more vigorous; the flame becomes

lighter in colour, and will deposit a black stain of Arsenic on the crucible lid when it is held in it. This Arsenic stain is soluble in a solution of Bleaching Powder; a similar stain produced by Antimony is not.

If a short piece of glass tubing is attached at *A* by a rubber connection, and then heated in a bunsen flame, a black deposit of Arsenic is formed in the cool part of the tube; this acts as a confirmatory test.

(2) *Reinsch's Test.* If a piece of pure Copper foil is boiled in a solution containing Arsenic and acidified with pure Hydrochloric acid, a grey deposit of Copper Arsenide, Cu_3As_2 , forms on the Copper. Mercury compounds also give this test,

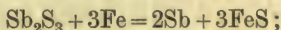
but may be distinguished by heating the dried Copper and its deposit in a clean test tube, when the black Arsenic (or white Arsenious Oxide) formed as a sublimate, is readily distinguished from globules of Mercury.

ANTIMONY.

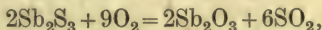
Symbol, Sb. (Stibium). Atomic Weight, 120.2.
Molecular Weight, 480.8.

Occurrence. Antimony occurs free to a very small extent in nature, and also combined in several minerals, the most important of which is Antimony Sulphide, *Stibnite*, Sb_2S_3 .

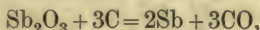
Preparation. Metallic Antimony is obtained from Stibnite, either by heating the ore with scrap Iron in graphite crucibles, when the Sulphur combines with the Iron, forming a slag of Iron Sulphide with molten Antimony underneath:



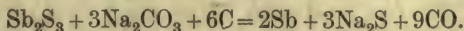
or, by mixing the ore with Charcoal and roasting it carefully to convert the Sulphide partially into Oxide:



and then mixing the residue with more Charcoal and Sodium Carbonate and heating the mixture strongly in a crucible. The Charcoal reduces the Oxide:



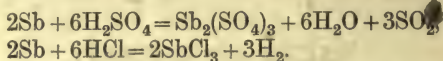
and the Sodium Carbonate and Carbon reduces the remaining Sulphide:



Properties. Antimony is a silvery-white metal, highly crystalline, and consequently very brittle. It remains untarnished in air, and, as it also takes a good polish, is used nowadays for many ornamental purposes.

When heated in air or Oxygen, it burns brilliantly, forming white fumes of Antimony Trioxide.

Dilute Sulphuric and Hydrochloric acids have no action on Antimony, but the hot concentrated acids form Antimony Sulphate and Chloride respectively :



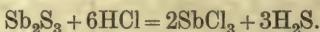
Antimony melts at 629°C ., and in the act of solidification expands. This property it imparts to its alloys, and these are used for making very fine and sharp castings. The most important are : *Type metal* (Lead 75, Antimony 20, Tin 5), and *Britannia metal* (Tin 140, Antimony 7, Copper 3).

Judged from its physical properties, Antimony—like Arsenic—possesses most of the characteristics of a metal, but in its chemical properties it is more like a non-metal ; it is usually called a metalloid.

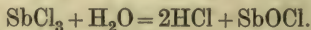
Antimoniuretted Hydrogen, Stibine SbH_3 . This gas is prepared, mixed with Hydrogen, by the action of nascent Hydrogen on any compound of Antimony. It closely resembles Arseniuretted Hydrogen in all its properties, and is equally poisonous. It decomposes more readily under the action of heat, and is generally not so stable.

CHLORIDES OF ANTIMONY.

Antimony Trichloride SbCl_3 . This substance is formed when Antimony powder is dropped into a jar of Chlorine gas or when the Trioxide, Trisulphide, or Antimony itself is boiled with strong Hydrochloric acid :



Properties. It is a colourless, crystalline deliquescent solid, readily soluble in water, with large quantities of which it forms, however, a white milky precipitate of Antimony Oxychloride, SbOCl :



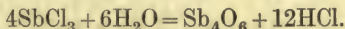
Antimony Pentachloride SbCl_5 is obtained by passing dry Chlorine over the heated Trichloride. It is a colourless

strongly-fuming liquid, which dissociates, on heating, like the corresponding Phosphorus compound, into the Trichloride and Chlorine gas.

OXIDES OF ANTIMONY.

Antimony forms three compounds with Oxygen : Antimony Trioxide, Sb_2O_3 , Antimony Tetroxide, Sb_2O_4 and Antimony Pentoxide, Sb_2O_5 . The first-named is the only one of any importance.

Antimony Trioxide Sb_4O_6 may be prepared by adding hot water to a solution of Antimony Trichloride and washing the precipitated Oxide with Sodium Carbonate solution to remove the free Hydrochloric acid :



It is a white powder which vaporizes without melting, and may be sublimed to purify it. It is only very slightly soluble in water, and the solution has no action on litmus.

Antimony Trioxide is insoluble in Nitric or Sulphuric acids, but dissolves readily in Hydrochloric acid, forming the Trichloride. It is also soluble in Tartaric acid and with a boiling solution of Potassium Hydrogen Tartrate (Cream of Tartar) yields Potassium Antimony Tartrate (Tartar Emetic). It burns in air, forming the Tetroxide, Sb_2O_4 .

OXY-ACIDS OF ANTIMONY.

No Oxy-acids of Antimony are known which are derived from Antimony Trioxide, but three Antimonic acids are formed by the solution of the Pentoxide, and these are analogous to the corresponding Arsenic and Phosphoric acids. They are Orthoantimonic acid, H_3SbO_4 , Pyroantimonic acid, $\text{H}_4\text{Sb}_2\text{O}_7$, and Metantimonic acid, HSbO_3 . The salts derived from them are called Antimoniates.

Tests for Antimony. Antimony compounds give an orange-coloured precipitate of Antimony Trisulphide, Sb_2S_3 when Sulphuretted Hydrogen is bubbled through a solution acidified

with Hydrochloric acid, and a similar solution gives a milky precipitate of SbOCl when added to much water.

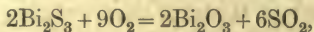
If Marsh's test for Arsenic is applied to Antimony compounds, a similar result is obtained, except that the black stain produced on the porcelain is insoluble in Bleaching powder solution.

BISMUTH.

Symbol, Bi. Atomic Weight, 208. Molecular Weight, 416.

Occurrence. Bismuth occurs most commonly as the metal itself. It is also found in combination with Oxygen in *Bismuth Ochre*, Bi_2O_3 , and with Sulphur in *Bismuth Glance*, Bi_2S_3 .

Preparation. Bismuth is prepared from its Sulphide by first roasting the ore in a current of air so as to form the Oxide :



and then reducing the Oxide to the metal by heating it with Charcoal.

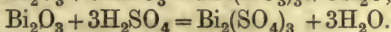
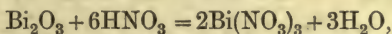
Properties. Bismuth is a lustrous white metal, very like Antimony. It is hard, brittle and crystalline, and is a poor conductor of electricity. It does not tarnish in dry air, but, when heated strongly in air or Oxygen, it burns, forming the Trioxide. The metallic properties, both physical and chemical, of Bismuth are much more pronounced than those of Arsenic or Antimony.

Bismuth is attacked slowly by Hydrochloric acid, forming the Trichloride, and with Sulphuric acid it forms a basic Bismuth Sulphate.

Bismuth readily forms alloys with other metals. These alloys are characterized by hardness and great fusibility. Many of the "fusible alloys" will melt in hot water, *e.g.* *Newton's metal* (Tin 3, Lead 5, Bismuth 8) melts at 94°C ., and *Wood's metal* (Tin 1, Lead 2, Cadmium 2, Bismuth 4) melts at 60°C .

These fusible metals are useful for making safety appliances in case of fire and for electrical fuse wire. Fireproof doors can be kept open by fusible plugs, which, when melted by a fire, allow the door to close automatically.

Compounds of Bismuth. Bismuth forms no compound with Hydrogen. It forms four Oxides, the Dioxide, Bi_2O_2 , Trioxide, Bi_2O_3 , Tetroxide, Bi_2O_4 , and Pentoxide, Bi_2O_5 . None of these Oxides are acidic, but the Trioxide dissolves readily in acids, forming the salts of Bismuth:



Bismuth forms several basic salts, of which the Oxychloride, BiOCl , and the Oxynitrate, BiONO_3 , are the best known.

Tests for Bismuth. Salts of Bismuth give a dark-brown precipitate of Bismuth Sulphide, Bi_2S_3 , with Sulphuretted Hydrogen in an acid solution. They also give a milkiness produced by the formation of the basic Chloride or Nitrate (BiOCl or BiONO_3) when added to a large quantity of water, and with Ammonium Hydrate they yield a white precipitate of Bismuth Hydrate, $\text{Bi}(\text{OH})_3$.

THE NITROGEN FAMILY OF ELEMENTS.

The properties of the group of elements—Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth—shew many points of similarity, particularly in their compounds. There is a regular change both in physical properties and the chemical properties of their compounds as the Atomic Weight increases. A table will shew some of the points:

	N.	P.	As.	Sb.	Bi.
Atomic weight	14.01	31.0	75.0	120.2	208
Sp. Gr. - -	(liquid) 1.026	1.82 - 2.25	5 approx.	6.62	9.8
Boiling point -	- 193° C.	287° C.	450°?	1350°	1435°

All the members of the group are tri-valent and penta-valent in their compounds.

Ammonia is a relatively strong base, Phosphine a feeble base, Arsine and Stibine shew no basic properties.

The acidic properties of the Oxides and the strength of the Oxy-acids diminish during the passage from Nitrogen to Bismuth.

In general the passage is from non-metallic Nitrogen to metallic Bismuth.

PRACTICAL EXERCISES.

Tests for Arsenic. Perform Marsh's test and Reinsch's test for Arsenic as described on page 300. Use a dilute solution of Arsenious Oxide in water.

Test for Antimony. Perform Marsh's test for Antimony. Use a solution of Antimony Oxide in Hydrochloric acid.

CHAPTER XXIV.

CARBON AND ITS COMPOUNDS.

CARBON.

Symbol, C. Atomic Weight, 12.00.

Occurrence. Carbon is found in its elementary state in nature in three allotropic forms: *Diamond*, *Graphite* and *Charcoal*. In combination with Oxygen it occurs as Carbonic acid gas in the air, and with Oxygen and metals as Carbonates, e.g. Calcium Carbonate, *Limestone*, CaCO_3 ; Copper Carbonate, *Malachite*, CuCO_3 , etc. In combination with Hydrogen it is found in numerous Hydrocarbons in oil wells and oil shales; it is also an essential constituent of all organic substances.

DIAMOND.

Occurrence. Diamonds are found, very sparsely distributed, all over the world. They are usually discovered in river gravels and surface deposits, which are the result of the breaking up or disintegration of rocks; the diamonds, being the hardest substance known, resist the breaking up process and remain in the gravel after the rest of the rock has been ground to powder and washed away.

The principal localities are India, Brazil, Australia and South Africa. At Kimberley in South Africa there is the largest diamond mine in the world. Here the diamonds are found in a circular pipe consisting of a mixture of various rocks cemented together by a hard bluish clay known as "blue".

earth." This pipe has apparently been thrust upwards through the volcanic rocks which surround it (Fig. 98). The "blue earth" is exposed to the action of the weather for one year, when it crumbles and is picked over for diamonds.

Varieties. Diamonds occur in many colours; the majority are colourless or very faintly yellow, but the admixture of minute quantities of various impurities colours them blue, pink, red and green. The usual crystalline form of the diamond is an octohedron, but its edges are always rounded, probably

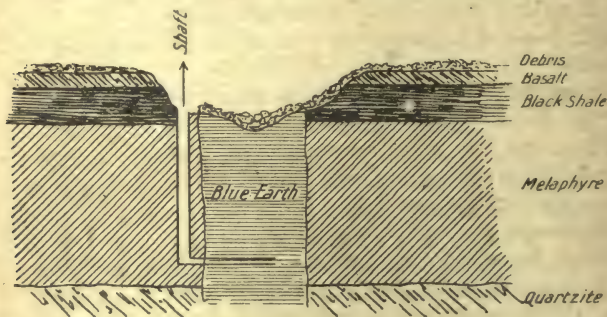


FIG. 98.—Diagrammatic section of the Kimberley Diamond Mine.

by attrition. The shapes of cut diamonds bear no relation to their crystalline form, the idea being to get the largest amount of reflected light so that the gem sparkles.

Some diamonds are almost black in colour; they are imperfectly crystallized, and are known as Black diamonds, Boart or Carbonado. They are used for drilling rocks and for cutting and polishing other stones.

Preparation. Natural diamonds have most probably been formed by the action of intense heat and enormous pressure for a very long time upon carbonaceous material, *e.g.* coal, shut up in rocks.

In his efforts to imitate Nature's methods, M. Moissan has been successful in producing small diamonds in the following way. Molten Iron will dissolve a considerable amount of Carbon at very high temperatures 3000° – 4000° C., but gives

it up on solidification. Moissan heated Iron and Sugar Charcoal in a Carbon crucible to a temperature of very nearly 4000°C . in his electric arc furnace. He then suddenly cooled the crucible and its contents by immersion in water or molten Lead. This sudden cooling solidified the outer layer of Iron, and the inner core was subjected to an enormous pressure, partly due to the contraction of the solid outer shell and partly to its own tendency to expand on solidifying. The Carbon, therefore, separated out under enormous pressure and at a high temperature, and, on dissolving the Iron away with Hydrochloric acid, small diamonds, some black, some colourless, were found in the residue.

Properties. The most striking properties of the diamond are its hardness—it is the hardest known substance—and its high refractive power—it has the highest refractive index known, viz. 2.45.

Diamonds are insoluble in all liquids.

When heated to a temperature of 2000°C . in an inactive atmosphere, such as Nitrogen gas, the diamond swells out into a black mass resembling Graphite. At temperatures below 1000°C ., it can be made to burn in air or Oxygen. If a small fragment of diamond is placed on a thin piece of Platinum foil *A* (Fig. 99) connecting two stout Copper leads *C*, through which a powerful electric current is passed, the whole being placed in a jar of Oxygen, as soon as the Platinum becomes red hot, the diamond burns brilliantly and Carbonic acid gas is produced.

Diamonds, when burnt, yield usually about .1 per cent. of impurity in the form of ash.



FIG. 99.—Combustion of diamond.

GRAPHITE.

Occurrence. Graphite occurs usually amongst rocks of the volcanic type, very widely distributed on the face of the earth. Large deposits are found in Ceylon and other parts

of India, Siberia, the United States, Canada, Bavaria and Bohemia. The English deposits, at Borrowdale in Cumberland, are practically exhausted. Graphite has also been found in a crystalline form in meteorites.

Preparation. Graphite always separates out when molten Iron solidifies, and considerable quantities are found sometimes at the base of blast furnaces; to this form the name "Kish" has been applied.

Acheson's Graphite is made at the Niagara Falls, by baking a mixture of ground coke and coal tar in suitable electrically-heated ovens.

Properties. Graphite is a soft dark-grey substance with a shining metallic lustre; it is soapy to the touch.

It is sometimes found crystallized in six-sided plates.

It is a good conductor of heat and electricity.

When heated to a temperature of 600°C . or 700°C ., in air or Oxygen, Graphite burns, forming Carbonic acid gas and leaving behind an ash consisting of Silica, Alumina and Oxide of Iron.

Dilute mineral acids have no action upon Graphite, but if a mixture of powdered Graphite and Potassium Chlorate is made into a thick paste with strong Nitric acid and warmed for several days, on washing with water, a yellow substance, called by Brodie, who first prepared it, Graphitic acid, is obtained.

The constitution of this substance is not quite clear, but it serves as a useful distinguishing test between Graphite and the other varieties of Carbon, which do not produce it under similar conditions.

Uses. It was, at one time, supposed that Graphite contained Lead, hence its commercial names of Plumbago and Black-Lead.

One of its principal uses is for the manufacture of "lead" pencils. Powdered Graphite is freed from grit and then mixed with various quantities of washed clay, according to the hardness required in the pencil. The stiff mixture is then pressed into the required shape and baked dry.

Mixed with an equal quantity of clay and sand, Graphite,

on account of its refractory qualities and good conductivity for heat, is used for making Plumbago crucibles. It is also used as a dry lubricant for machinery, and as a coating for Iron to prevent the formation of rust.

Graphite poles are used in many modern electrolytical processes, *e.g.* the electrolysis of Salt, on account of its being a good conductor of electricity.

AMORPHOUS CARBON.

Whenever an organic substance is heated, out of contact with air, Amorphous Carbon is usually left behind in one form or another. Various names are given to it—*Charcoal*, with prefixes suggesting the substance from which it has been derived (*e.g.* wood Charcoal), *Lampblack*, *Coke* or *Gas Carbon*.

It is found in nature, mixed with many impurities, in the form of *Coal*.

The purest form of Amorphous Carbon is obtained by the destructive distillation of Sugar, and is called Sugar-Charcoal.

Lampblack. This form is made by burning substances rich in Carbon, such as Turpentine, Petroleum or Tar, in a limited quantity of air, so that the maximum amount of smoke is produced. This smoke is led into chambers containing suspended coarse blankets, on which the Lampblack is deposited. It is a very pure form of Carbon, yielding, as a rule, only about 1.5 per cent. of Hydrogen. It is used for printer's inks and black paint.

Wood Charcoal. In places where wood is abundant, such as Norway and Sweden or parts of England, Wood Charcoal can be made by stacking up small logs and billets of wood in the form of a pile and covering it over with sods and turf to prevent free access of air. A small opening is left in the centre for the purpose of making a draught, and the pile is lit at the bottom. It is carefully watched and allowed only to smoulder away slowly without burning brightly, and eventually, when cold, a heap of Wood Charcoal is left. It is a very wasteful process, only about 15 per cent. of the wood remaining as Charcoal.

Wood Charcoal is used as a fuel, in the manufacture of Iron and Steel, for making Gunpowder and for filters.

Animal Charcoal. When bones are heated strongly in Iron retorts, a substance called Animal Charcoal is left behind. It is a very impure form of Carbon, containing, roughly, 90 per cent. of impurities, but it possesses many of the most valuable properties of Charcoal in a highly marked degree and is made use of in various ways.

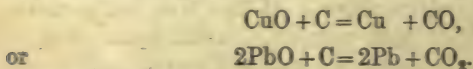
Coke or Gas Carbon is left behind in the destructive distillation of Coal. It is a comparatively pure form, containing over 90 per cent. of Carbon. It is very much used as a fuel and also, being a good conductor of electricity, for the making of Carbon rods for arc lights.

Properties of Amorphous Carbon. The various forms are usually black in colour and soft in texture, but some kinds of Coke are grey, and so hard that they do not mark paper or soil the fingers when handled.

Ordinarily Charcoal is unacted upon by air, but, when the temperature is raised up to about 400°C . to 500°C ., it burns, uniting with the Oxygen to form Carbon Dioxide.

In a finely divided condition, however, Carbon combines at ordinary temperatures with Oxygen, to a sufficient extent and evolving so much energy as to take fire.

On account of its affinity for Oxygen, Charcoal is a very good reducing agent. When a mixture of Carbon and a metallic Oxide is heated strongly, the Oxygen combines with the Carbon and the metal is left behind; either of the following reactions may take place:



This reaction is made use of in processes for obtaining many of the metals, *e.g.* Iron, Copper, Zinc, Lead, from their ores, and also as a means of identification of many metals in ordinary analysis. In this latter case, it is often of great help to add a little Sodium Carbonate to the metallic salt before heating it on the Charcoal before the blowpipe. By this addition, as soon as the mass becomes

molten, the Carbonate of the metal is first formed. This is quickly changed by the heat into the Oxide, which is, in most cases, much more readily reducible than the original salt.

The specific gravity of amorphous Carbon depends greatly upon the temperature at which it was made, varying from 1.45 to 1.7. Although in itself heavier than water, a piece of Charcoal will float on it, because it is buoyed up by the air in its pores.

The presence of this air in the pores of a lump of Charcoal may be shewn by anchoring it (Fig. 100) by a weight in a jar full of water and then pumping out the air from the jar above the water; under the reduced pressure, the air escapes from the pores of the Charcoal in the form of bubbles.



FIG. 100.—Air absorbed in Charcoal.



FIG. 101.—Absorption of Ammonia gas by Charcoal.

Freshly-made Charcoal has a remarkable power of absorbing gases. If such a piece of Charcoal, or one recently heated to expel the air, is placed in a tube full of Ammonia gas (Fig. 101), over Mercury, the liquid rises nearly to the top of the tube owing to the large quantity of Ammonia which is absorbed by the Charcoal. This process is sometimes called *Adsorption*, meaning that the gas adheres in some unknown way to the surface of the Charcoal.

One c.c. of freshly-prepared coconut Charcoal at 0° C. absorbs, according to Hunter, 171 c.c. of Ammonia, 68 c.c. of Carbon Dioxide, 18 c.c. of Oxygen and

15 c.c. of Nitrogen. These figures are very much increased at low temperatures ; also, it will be noticed that, the nearer the gas is to its liquefying point, the more it is absorbed by the Charcoal. It is therefore often stated that the gases are liquefied on the surface of the Charcoal ; at any rate, the "condensed" gas is much more active than the gas in its ordinary condition.

As an example of this, if a lump of Charcoal, saturated with Sulphuretted Hydrogen gas, is lowered into a jar of Oxygen, the two gases unite with the evolution of so much heat that the Charcoal takes fire.

Again, because the "condensed" Oxygen in its pores is so active, Charcoal is used for keeping sewers "sweet," for preventing the soil or fibre in plant pots, which have no drainage, from becoming foul, and for filtering drinking water.

Charcoal possesses also the power of absorbing solids and liquids. If some Charcoal is placed in solutions of Litmus, Tea or Indigo, and the mixture is shaken for a time and then filtered, the filtrate is found to be quite colourless.

This property is made use of in the removal of the brown colouring matter from raw sugar. The brown solution is boiled for some time with animal Charcoal. This removes the colouring matter and White Sugar crystallizes out from the clear syrup which is left.

Besides its union with Oxygen, which has already been spoken of, Carbon unites directly with many elements at high temperatures, *e.g.* with Hydrogen to form Acetylene, with Nitrogen to form Cyanogen, with Sulphur to form Carbon Disulphide, and with metals to form Carbides, of which latter compounds Calcium Carbide is the most important.

Coal. Under this name are included a large number of different kinds of substances containing carbonaceous matter with Hydrogen, Oxygen, etc.

All the varieties have been formed—geologists say—by the gradual decomposition of vegetable tissues. In many of the softer varieties, their vegetable origin is quite clear, they are so little changed ; whilst among the harder kinds, the imprints of fern leaves and the presence of fossil seeds, spores,

and roots leave no doubt as to the source from which the coals originated.

From vegetable tissue, gradual decomposition has produced first Peat, then Lignite, Bituminous or Soft Coal, Anthracite or Hard Coal and finally perhaps Graphite. These varieties pass, the one from the other, by insensible gradations, the percentage of Carbon becoming greater, and that of volatile matter becoming less, from Peat to Anthracite.

Bituminous Coal is the one used for ordinary heating purposes. It contains a large amount of volatile matter, burns with a long yellow flame, and gives off a fair amount of heat. A variety of this Coal, called "Cannel Coal," because it burns like a candle, is used entirely for gas-making, owing to the large percentage of highly luminous gas evolved on heating it.

Anthracite Coal is very hard, dense and brittle; it has a very low percentage of volatile Hydrocarbons, and burns with a short flame, giving off a large amount of heat.

COMPOUNDS OF CARBON AND HYDROGEN.

Carbon forms a very large number of compounds with Hydrogen. Most of these, with their derivatives, are studied under the name of Organic Chemistry, a branch of the science originally intended to embrace substances which could only be formed by the agency of "life." This distinction no longer holds good, as most of the so-called Organic Substances have been made synthetically by Inorganic processes.

Only three Hydrocarbons will be studied here: Methane, CH_4 , Ethylene, C_2H_4 and Acetylene, C_2H_2 .

METHANE OR MARSH GAS.

Formula, CH_4 . Molecular Weight, 16.0.

Occurrence. This gas derives its name of Marsh gas from the fact that it is the principal constituent of the bubbles of gas which rise to the surface when the mud at the bottom of

a pond or a stagnant pool is disturbed. It is probably the product of the gradual decay of vegetable matter in a limited supply of air. This is the cause of its presence in Coal, where it is often absorbed or occluded under considerable pressure. When the atmospheric pressure is low, more of this gas makes its way out of a Coal seam into the workings; hence the warnings against "*fire-damp*," as it is called, when the barometer is low.

Large quantities of Methane escape from the petroleum springs of Russia and the United States, where it is called *Natural gas*.

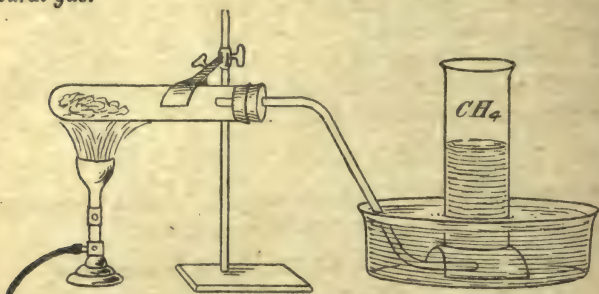
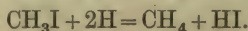


FIG. 102.—Preparation of Methane.

Preparation. To prepare Methane, some Sodium Acetate must first be deprived of water by melting it in an Iron dish, and then mixed with three times its weight of Soda-Lime or Caustic Soda. The mixture is placed in a Copper retort or hard-glass test tube, and heated strongly, the evolved gas being collected over water:

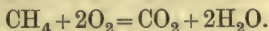


The gas prepared by this method is not very pure, and always burns with a luminous flame; if the pure gas is required, Methyl Iodide is reduced by nascent Hydrogen, formed by the action of a Zinc-Copper couple on water. This method of preparation belongs really to the domain of Organic Chemistry:



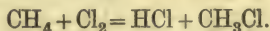
Properties. Pure Methane has no colour. It is about half as heavy as air, and dissolves only to a small extent in water.

It burns, when pure, with a pale blue non-luminous flame, forming Carbon Dioxide and water :

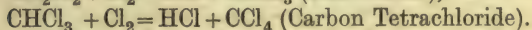
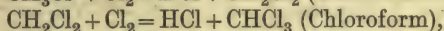


Ignition takes place at a temperature of about 700°C . Methane requires twice its volume of Oxygen or ten times its volume of air for complete combustion, and such a mixture is violently explosive. Diluted with more air, the explosion is less violent, but a mixture of Methane with 20 times its volume of air will explode ; hence the danger of fire-damp.

A mixture of equal volumes of Methane and Chlorine in *diffused daylight* changes gradually with the formation of Methyl Chloride and Hydrochloric acid :

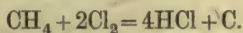


Further additions of Chlorine cause the gradual replacement of all the Hydrogen atoms, one by one, thus :



Such displacement of one or more atoms in a compound by equivalent atoms is called *substitution*, and indicates that the original compound is a saturated one.

If a mixture of Methane and Chlorine in the proportion 1 : 2 is exposed to *direct sunlight*, an explosion occurs, black particles of Carbon being set free :



A similar reaction occurs if a lighted taper is applied to the mixture.

Composition and Formula. The experiment just described indicates the presence of Carbon and Hydrogen (since Hydrochloric acid is known to contain Hydrogen) in Methane, and the proportions of these elements present are determined by eudiometric analysis.

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A known volume of Methane is taken in a eudiometer, a measured excess of Oxygen is added and a spark passed. After cooling, the volume of the gases which remain, which consists of Carbon Dioxide and Oxygen, the Water having condensed, is read, a little strong Caustic Potash solution is inserted into the tube to absorb the Carbon Dioxide, and, after a time, the volume of Oxygen which was added in excess is read. An example will enable the results to be seen more clearly :

Volume of Methane taken	-	-	-	= 20 c.c.
Volume after adding Oxygen	-	-	-	= 90 c.c.
Hence volume of Oxygen added	-	-	-	= 70 c.c.
Volume after explosion	-	-	-	= 50 c.c.
Volume after adding Caustic Potash	-	-	-	= 30 c.c.
Hence volume of Carbon Dioxide formed	-	-	-	= 20 c.c.
And volume of Oxygen used for burning the				
Methane	-	-	-	= 40 c.c.

Collecting these results, 20 c.c. of Methane require 40 c.c. of Oxygen for complete combustion, and form 20 c.c. of Carbon Dioxide and an unknown quantity of Water.

Whence, by Avogadro's Hypothesis, one molecule of Methane requires two molecules of Oxygen, *i.e.* O_2 , to burn it, and forms one molecule of Carbon Dioxide CO_2 .

Now, since one molecule of Carbon Dioxide contains one atom of Carbon, there can only have been one atom of Carbon in the original molecule of Methane. Hence its formula may be written CH_4 .

Again, one molecule of Carbon Dioxide requires one molecule of Oxygen (O_2) for its formation ; therefore, of the four atoms of Oxygen required to burn the molecule of Methane, two must have been used for burning the Hydrogen in the molecule.

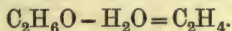
But two atoms of Oxygen will burn four atoms of Hydrogen. Therefore, there must be four atoms of Hydrogen in the molecule of Methane, and its formula is therefore CH_4 .

ETHYLENE OR OLEFIANT GAS.

Formula, C_2H_4 . Molecular Weight, 28.0.

Occurrence. Ethylene is found amongst the gases given off from oil wells, and also forms about 5 or 6 per cent. of Coal gas.

Preparation. When powerful dehydrating agents, such as Sulphuric or Phosphoric acids, act upon Alcohol, a molecule of water is taken away from each molecule of the Alcohol, leaving Ethylene :



To prepare it, five volumes of Sulphuric acid are gradually mixed with one volume of Alcohol in a beaker kept cool by

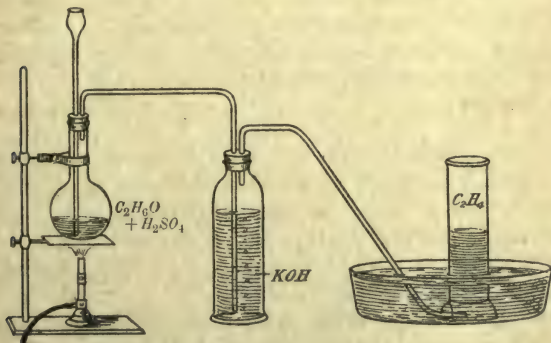


FIG. 103.—Preparation of Ethylene.

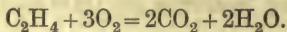
being immersed in water. The mixture is placed in a flask (Fig. 103) and heated to a temperature of $160^{\circ} C.$, when Ethylene gas is evolved.

Owing to the partial carbonization of the Alcohol, secondary actions occur, the Carbon acting as a reducing agent on the Sulphuric acid, producing Sulphur Dioxide. This gas is stopped by the wash-bottle containing Caustic Potash, and the Ethylene is collected over water.

Properties. Ethylene is a colourless gas with a pleasant ethereal smell. It dissolves to some extent in water—100 c.c.

of water dissolve 25 c.c. of the gas at 0° C., and it is very much more soluble—13 times—in Alcohol.

It burns in air or Oxygen with a highly luminous but rather smoky flame, and needs three times its volume of Oxygen for complete combustion :



A mixture in these proportions is very explosive.

At a high temperature, Ethylene decomposes into Carbon and Hydrogen. This may be shewn by passing the gas through a bulb of hard glass heated in the blowpipe flame, when a black deposit of Carbon is formed in the bulb.

Ethylene gas combines directly, under normal conditions, with Chlorine and Bromine, forming Ethylene Dichloride, $\text{C}_2\text{H}_4\text{Cl}_2$, and Ethylene Dibromide, $\text{C}_2\text{H}_4\text{Br}_2$. These two substances are both oily liquids. Hence the old name of *Olefiant gas* for Ethylene.

Products of this kind, where atoms of an element are added directly to the molecule of a compound, are called *addition products*, and their formation indicates that the original compound is unsaturated.

Formula. By eudiometric analysis (see Methane), it is found that one volume of Ethylene requires three volumes of Oxygen for complete combustion, and forms two volumes of Carbon Dioxide and some Water.

Hence, by Avogadro's Hypothesis, one molecule of Ethylene requires three molecules of Oxygen, *i.e.* O_6 , to burn it completely, and forms two molecules of Carbon Dioxide.

Each molecule of Carbon Dioxide contains one atom of Carbon, and therefore the original molecule of Ethylene must have contained two atoms of Carbon.

Also the two Carbon Dioxide molecules require four Oxygen atoms for their formation, leaving two Oxygen atoms to burn the Hydrogen contained in one molecule of Ethylene. But two Oxygen atoms will burn four atoms of Hydrogen.

Hence the formula for Ethylene must be C_2H_4 .

ACETYLENE.

Formula, C_2H_2 . Molecular Weight, 26.0.

Preparation. Acetylene was synthetically prepared by Berthelot, by passing Hydrogen gas through a globe (Fig. 104)

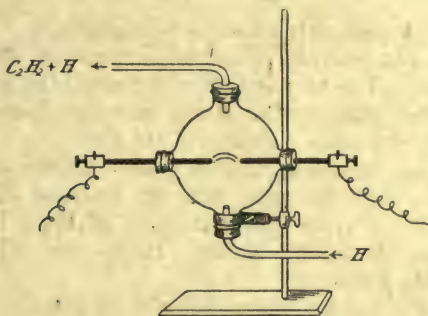


FIG. 104.—Synthesis of Acetylene.

containing two Carbon rods, between which a strong current is passing in the form of an arc light. At this high temperature, union takes place between the Carbon and Hydrogen, and Acetylene is carried away in the current of Hydrogen.

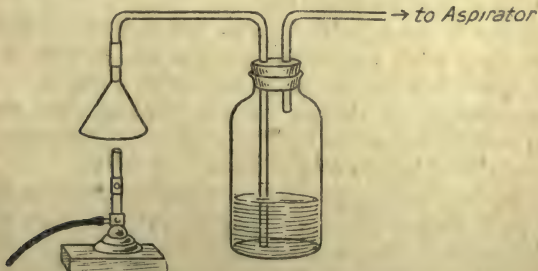


FIG. 105.—Acetylene from Coal Gas.

Acetylene gas is also formed by cooling a Coal-gas flame. This is best done by allowing a bunsen burner to "strike
o.c. X

back." Then, if the products of combustion are drawn by means of an aspirator (Fig. 105) through a solution of Ammoniacal Cuprous Chloride, a red precipitate of Copper Acetylide indicates the formation of Acetylene.

The most convenient method for preparing Acetylene in the laboratory is by the action of water upon Calcium Carbide. Some fragments of this substance are placed at the bottom of a bottle (Fig. 106), fitted as in the diagram. Coal gas is first

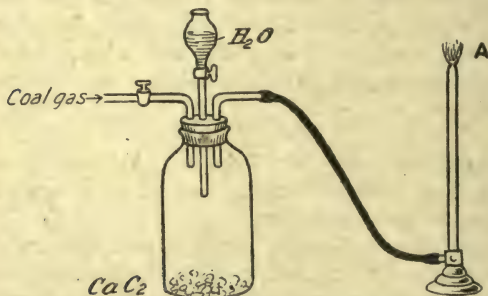
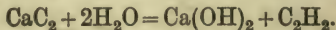


FIG. 106.—Preparation of Acetylene.

passed through to drive out all the air, and the gas is ignited at the jet *A*. Water is then admitted slowly through the dropping funnel, and the Coal gas turned off; the flame at the jet becomes much smaller and more brilliant owing to the formation of Acetylene. The gas may be collected over water if necessary, care being taken, as it is poisonous. A white deposit of Calcium Hydrate remains in the bottle:



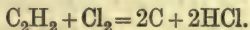
Properties. Acetylene is a colourless gas which, when pure, has a pleasant ethereal smell, but, as ordinarily prepared, the impurities present give it a very offensive odour.

It dissolves fairly well in water—100 c.c. of water will absorb 173 c.c. of Acetylene at 0° C.—and is much more soluble in Alcohol.

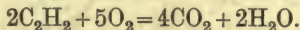
It is poisonous, if inhaled in the pure state, but less so than

Carbon Monoxide. Moreover, it is usually detected readily by its smell.

If Chlorine is allowed to enter a jar of Acetylene over water, a flash occurs as each bubble breaks; Carbon is deposited in the form of soot, and the water rises till it eventually fills the jar, owing to the solubility of the Hydrochloric acid gas which is produced :



Acetylene burns in air with a luminous but very smoky flame. If the gas is burnt from a proper Acetylene burner, which has a very small aperture, the flame is small but intensely luminous, and the light is often used for purposes of illumination :



The high luminosity of the gas coupled with its ready preparation from Calcium Carbide, has led to a very wide use of it for bicycle and motor lamps.

Oxy-acetylene blowpipes, which burn a mixture of Oxygen and Acetylene, under pressure, through a specially constructed nozzle, are used for producing very high temperatures over a limited area, in processes like the welding or brazing together of pieces of Iron. The flame is intensely hot, somewhere in the neighbourhood of 2500°C . It is hotter than the Oxy-Hydrogen flame, which has a temperature round about 2000°C .

Acetylene, as seen from its formation by means of the electric arc, is stable at high temperatures, but if passed through a glass tube heated to about 800°C ., it splits up, depositing Carbon, just as Ethylene does.

When Acetylene gas is passed through an Ammoniacal solution of Cuprous Chloride, a reddish-brown precipitate of Copper Acetylide (possible formula, $\text{Cu}_2\text{O} \cdot \text{C}_2\text{H}_2$) is formed, and this forms a very delicate test for the gas. When this precipitate is dried, C_2Cu_2 , which is also called Copper Acetylide, is left, a substance which explodes when warmed slightly or when struck.

Formula. By a precisely similar method to those used for Methane and Ethylene, the formula C_2H_2 has been arrived at for Acetylene.

PETROLEUM.

Crude Petroleum, or Rock-oil, as it is sometimes called, occurs underground in many places, notably the Baku district of Russia, in most of the States which comprise the United States, in Mexico, India, Canada, Australia, Trinidad, etc., etc. Sometimes it comes to the surface without any assistance, at others, a "bore hole" is sufficient to cause it to rise as a spring, whilst in some places it has to be pumped to the surface.

It consists of a complex mixture of Hydrocarbons, and though crude Petroleum is used as a fuel in many industries and is beginning to be used largely in steamships, the oil is usually refined, before use, by fractional distillation.

The following table shews the names applied to the various fractions, their boiling points and uses :

Name.	Boiling Point.	Uses.
Petroleum Ether - -	50°- 60° C.	Solvent, fuel.
Petrol - - -	70°- 90° C.	Solvent, fuel.
Naphtha - - -	90°-120° C.	Solvent, fuel.
Benzene or Benzoline -	110°-140° C.	Solvent.
Kerosene or Paraffin -	150°-300° C.	Fuel, illuminant.

The residue after those fractions have been taken out, if distilled further, yields lubricating oils, Vaseline and Paraffin Wax.

An oil, similar to crude Petroleum, is obtained when the oil shales of Mid-Lothian in Scotland are heated, and similar shales in New South Wales yield a large quantity of a Petroleum-like oil when subjected to *dry distillation*, as the process is called.

COAL GAS.

When powdered Coal is heated in a hard-glass test tube (Fig. 107) and the volatile products are led into a glass bottle to be cooled, and out of it through a tube, the gas which comes out consists of impure Coal gas, and, if lighted, burns with a smoky flame. In the bottle a black oily liquid—Coal tar—condenses and above it a yellowish liquid, which is strongly alkaline and smells of Ammonia gas. Ammonia can also be

COAL GAS

recognized in the gas which issues from the jet by the fact that it turns red litmus paper blue. This gas will also be

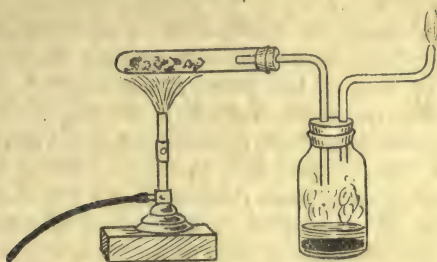


FIG. 107.—Dry distillation of Coal.

Lead Acetate solution on a filter paper, shewing that Sulphuretted Hydrogen is present.

The main products of the destructive distillation of Coal are : (1) Coke, (2) Coal Tar, (3) Benzol and Toluol, (4) Ammonia, (5) Sulphuretted Hydrogen, (6) Purified Coal Gas.

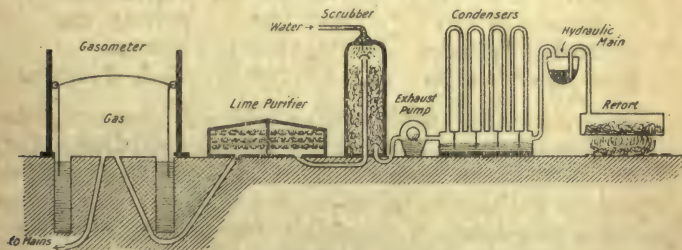


FIG. 108.—Diagrammatic section of Coal Gas Works.

In the manufacture of Coal gas, the object is to get rid of the impurities (2), (3), and (4), and this is effected somewhat as shewn in the diagram (Fig. 108).

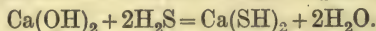
Bituminous or Cannel Coal is heated in D-shaped earthenware retorts, Coke is left behind and the evolved gases pass first into the "hydraulic main," where a portion of the tar is condensed, under which the pipe from the retort dips. The gas passes next up and down a series of long iron pipes, where it is well

cooled by the surrounding atmosphere, and here the rest of the coal tar condenses.

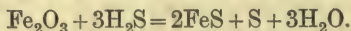
An "exhaust pump" then draws the gases along and forces them through a "scrubber." This is a tower filled with broken bricks or coke down which water is constantly trickling, and here all the Ammonia is taken away from the gas, forming Ammonia liquor, a very valuable bye-product.

The gas passes next into the purifiers, of which only one is shewn in the diagram. These are provided with perforated shelves, over which is strewn either slaked Lime or Hydrated Ferric Oxide. Either of these substances will remove the Sulphuretted Hydrogen from the gas.

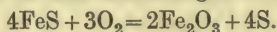
In the case of the Lime, Calcium Hydrosulphide is formed, and the Lime cannot be recovered and is "spent":



In the case of Ferric Oxide, Ferrous Sulphide and free Sulphur are formed:



The Ferrous Sulphide can be made into Ferric Oxide again by exposure to the air and so used again:



The gas finally passes into the gasometers, where it is stored.

One ton of gas coal yields approximately 10,000 cubic feet of gas, 1400 lbs. of Coke, 120 lbs. of Tar and 20 gallons of Ammonia liquor.

A well purified Coal gas contains the following constituents:

	Per cent.	
Hydrogen - - -	49	These gases give out, on burning, great heat but little light.
Methane - - -	35	
Carbon Monoxide -	7	
Ethylene, Acetylene, etc. - - -	5	These gases give out all the illumina- tion.
Nitrogen and Carbon Dioxide - - -	4	
		Impurities.
	100	

CARBON AND OXYGEN.

Carbon forms two compounds with Oxygen, both of which are gaseous at ordinary temperatures and of considerable importance. They are called Carbon Dioxide, CO_2 and Carbon Monoxide, CO .

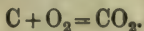
CARBON DIOXIDE OR CARBONIC ACID GAS.

Formula, CO_2 . Molecular Weight, 44.0.

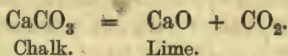
History. Carbon Dioxide was first recognized as a gas distinct from air by van Helmont in the seventeenth century. He shewed that it was formed during the burning of Charcoal and the fermentation and decay of organic matter. He recognized its presence in the mineral waters at Spa in Belgium and in the Grotto del Cane at Naples. Black (1755) proved that it was contained in the Alkaline Carbonates, or Mild Alkalies, as they were then called, and gave it the name of "fixed air" because it was combined or fixed in these compounds. Lavoisier first proved that it was an Oxide of Carbon.

Occurrence. Carbon Dioxide is a constant constituent of air to the extent of 4 parts in 10,000. It is found dissolved in all river and spring waters, in the latter to such an extent sometimes, that the water sparkles or effervesces, owing to the escape of the gas. It is given off in large quantities from volcanoes in eruption, and often issues from vents or cracks in the ground in volcanic districts, such, for example, as the Poison Valley in Java and the Grotto del Cane in Naples. It is often found at the bottom of old wells and deep pits, produced probably by the decay of vegetable matter; hence such places should always be tested, by lowering into them a lighted candle, before any attempt at exploring them is made.

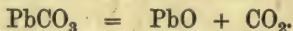
Preparation. (1) Carbon Dioxide is formed when Carbon is burnt in *excess* of air or Oxygen:



(2) All metallic Carbonates, with the exception of those of the Alkali metals (Na, K, etc.), decompose when strongly heated, yielding the Oxide of the metal and giving off Carbon Dioxide :

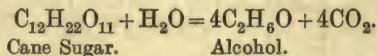


Chalk. Lime.



White Lead. Litharge.

(3) Carbon Dioxide is always evolved during the fermentation of Sugar or Starch by yeast. This is the cause of the effervescence of drinks like bottled Ale and Ginger beer and also of the rising of the dough in the first stage of bread-making. With Sugar the equation is

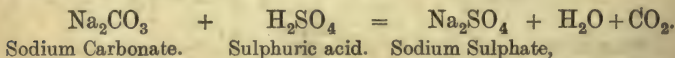


Cane Sugar.

Alcohol.

It will be noticed that Alcohol is produced by the fermentation of Sugar ; hence this liquid is always present in drinks like Ginger beer and Herb beer, which have been caused to ferment in the bottle.

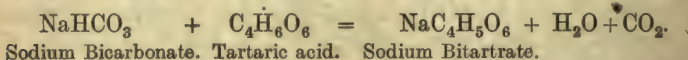
(4) Carbon Dioxide gas is evolved when any metallic Carbonate is acted upon by an acid. Examples :



Sodium Carbonate.

Sulphuric acid.

Sodium Sulphate,



Sodium Bicarbonate.

Tartaric acid.

Sodium Bitartrate.



Marble.

Hydrochloric acid.

The second of the above equations represents the action which takes place during the effervescence of a Seidlitz powder, the blue and white packets containing, separately, the Bicarbonate and Tartaric acid mixed with other chemical substances of a medicinal nature.

The ordinary preparation of the gas is by the method shewn in the last of the above equations. The experiment may be performed by putting lumps of Marble in a Woulff's

bottle (Fig. 109) and acting upon them with dilute Hydrochloric acid, or a Kipp's apparatus (Fig. 110) may be used, by which a supply of the gas is always ready to hand. In both cases the Carbon Dioxide is usually collected by downward displacement, though it may be collected over water, as it is not very soluble in this liquid.

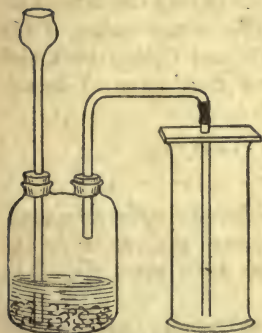


FIG. 109.—Preparation of Carbon Dioxide.

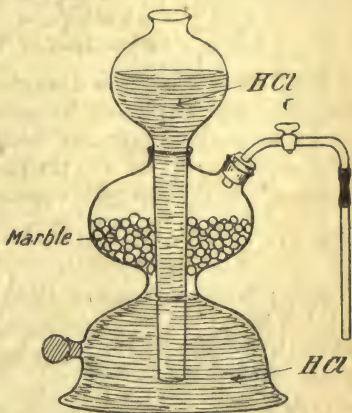


FIG. 110.—Kipp's apparatus for preparing Carbon Dioxide.

Properties. Carbon Dioxide is a colourless gas with no smell. It is not exactly a poisonous gas, though it will not support life, but, even a comparatively small percentage of the gas in air exercises a lowering effect on the vitality of the system. It is chiefly the presence of this gas in the "after damp," *i.e.* the products of combustion of a coal-mine explosion, which makes it so dangerous to life.

Carbon Dioxide is a heavy gas, being $1\frac{1}{2}$ times as heavy as air. This property, in conjunction with the fact that it is a bad supporter of combustion and immediately extinguishes a flame, may be exhibited by many experiments.

- (1) It may be "ladled," by means of a small beaker suspended by a string, from one beaker to another, just as water is raised from a well by a bucket.

- (2) Soap bubbles, inflated with air, can be made to float on a pneumatic trough filled with the gas.
- (3) The gas may be poured from a large jar, down a long cardboard gutter leading into a beaker in which a short piece of burning candle is placed; the light is at once extinguished.

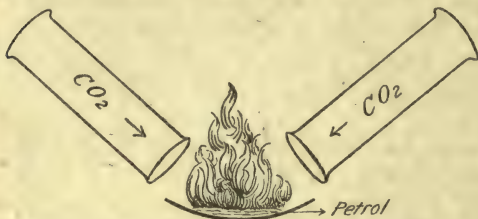


FIG. 111.—Exinction of flame by Carbon Dioxide.

- (4) If some Petroleum or Turpentine is placed in a shallow Iron dish and set alight, it can be at once extinguished by pouring the Carbon Dioxide, from two jars simultaneously, upon it (Fig. 111).

The fact that Carbon Dioxide extinguishes fires is made use of in small "chemical fire engines." An example is seen in the diagram (Fig. 112). The main body of the instrument is filled with a saturated solution of Sodium Carbonate; supported inside is a glass tube filled with sufficient Sulphuric acid to liberate most of the Carbon Dioxide from the Carbonate. In cases of fire, by giving the plunger *A* a sharp blow on the ground, the acid tube is broken, Carbon Dioxide is liberated in large volumes, and, if the instrument is held pointing slightly downwards, the pressure of the evolved gas drives a mixture of Carbon Dioxide and liquid out of the nozzle.

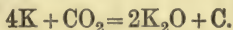
Although Carbon Dioxide is a non-supporter of combustion in the ordinary way, certain heated metals possess the power to split it up, uniting with the Oxygen and liberating the Carbon.

If a strip of burning Magnesium ribbon is lowered into a jar

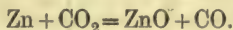
full of Carbon Dioxide, it continues to burn with a spluttering noise, leaving a white ash of Magnesium Oxide, with black specks of Carbon upon it:



If well dried Carbon Dioxide is passed over some shavings of Potassium, Calcium or Magnesium contained in a strongly heated hard-glass bulb, a similar decomposition takes place:



With Iron or Zinc, in a similar apparatus, the Carbon Dioxide is reduced to the Monoxide:



Carbon Dioxide gas dissolves fairly readily in water; one volume of water at 15°C . dissolves about one volume of the gas, and, by Henry's Law (p. 84), it is much more soluble under increased pressure. Liquids like "soda water" are merely solutions of the gas, under pressure, and effervesce when the pressure is released by extracting the cork. A precisely similar action occurs with liquids like beer, champagne, ginger beer, etc., which have been bottled during fermentation.

The dried gas or liquid Carbon Dioxide has no effect on dry litmus paper; however, if the paper is damped, the blue colour changes to red, but recovers its original blue colour on drying.

The solution, therefore, is of a weak acid nature, and is supposed to contain Carbonic acid, H_2CO_3 , but the acid itself has never been isolated, as it decomposes at once, on evaporation, into Carbon Dioxide and Water:

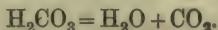
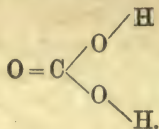


FIG. 112.—Fire Extinguisher.

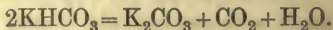
Carbonic acid is a di-basic acid, and its formula may be written



Its salts are called Carbonates or Bicarbonates, according as both or one of the Hydrogen atoms are replaced by metals. Thus, Na_2CO_3 is Sodium Carbonate and NaHCO_3 is Sodium Bicarbonate.

The Carbonates are stable salts at ordinary temperatures, but most of them yield Carbon Dioxide on heating, as has already been seen.

The Bicarbonates are much less stable than the Carbonates, and split up, on gently heating, into the Carbonates, Carbon Dioxide and Water :



The formation of the Carbonates and Bicarbonates of Sodium and Potassium is readily performed by leading Carbon Dioxide gas into solutions of Caustic Soda or Caustic Potash. For the Carbonate the equation is

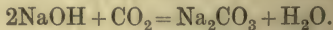
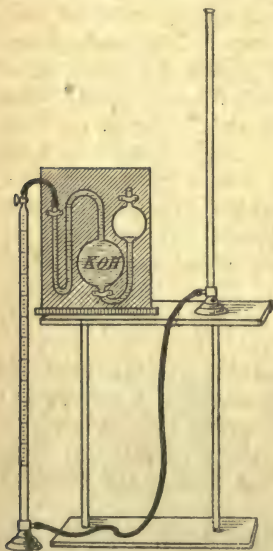
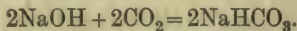


FIG. 118.—Analysis of a gas containing Carbon Dioxide.



For the Bicarbonate, twice the amount of Carbon Dioxide is required ; hence the prefix Bi- :



The absorption of Carbon Dioxide by Caustic Potash or Soda is made use of in the determination of the proportion

of the gas present in a gaseous mixture which contains it. A measured volume of the mixture is placed in a Hempel's burette (Fig. 113), and a strong solution of Caustic Potash is placed in the first bulb. The gas is forced over into the bulb and left there for about one minute, then, on returning the gas to the burette, the loss in volume measures the quantity of Carbon Dioxide present.

Liquid and Solid Carbon Dioxide. Carbon Dioxide gas can be condensed to a liquid by the application of cold or great pressure or both. The liquefaction temperature under 760 mm. pressure is -78°C . At 15°C ., a pressure of 52 atmospheres (780 lbs. per sq. inch) will cause it to liquefy, but at or above 32°C ., no amount of pressure will change it into a liquid. This temperature is called the *critical temperature* of the gas (p. 176).

Liquid Carbon Dioxide is made in large quantities from the waste gas which rises from the vats of fermenting beer. The gas is washed to purify it, and pumped into steel cylinders (bombs) by powerful compression pumps. These bombs are used for the manufacture of aerated water, and are called Sparklets.

Liquid Carbon Dioxide is colourless and very mobile. It floats on water without mixing with it.

If liquid Carbon Dioxide is allowed to escape from the nozzle of a "bomb" into the air, it solidifies, as a snow-like solid, owing to the absorption of the Latent Heat of Evaporation. This "Carbonic acid snow" can be collected by tying a small canvas bag over the nozzle and holding the "bomb" upside down.

Both liquid and solid Carbon Dioxide are used for the production of low temperatures by their rapid evaporation.

The solid "snow" dissolves in Ether, and, as the solution evaporates, a temperature of about -110°C . can be obtained, and it serves as an excellent freezing mixture. Many gases can be liquefied by passing them through tubes immersed in the solution.

The Composition and Formula of Carbon Dioxide.

(1) *By Weight.* Many accurate experimenters have determined the combining ratio of Carbon to Oxygen in Carbon

Dioxide, by burning pure specimens of each of the three varieties of Carbon—Sugar Charcoal, Graphite and Diamond—in a stream of pure Oxygen, and absorbing the Carbon Dioxide formed by means of Caustic Potash. All three varieties gave precisely similar results: 1 gram of Carbon required for complete combustion 2.666 grams of Oxygen or, to put it differently, 8 grams of Oxygen unite with precisely 3 grams of Carbon. Now the density of Carbon Dioxide is 22 ($H=1$); hence its molecular weight is 44, and this must therefore be made up of 12 parts of Carbon to 32 parts of Oxygen.

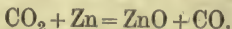
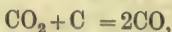
As this is the least weight of Carbon present in the molecule of any of its compounds, the Atomic Weight of this element is reckoned as 12.

(2) *By Volume.* The composition of Carbon Dioxide by volume is determined by a precisely similar method to the one used for Sulphur Dioxide (p. 227), substituting Carbon for Sulphur.

CARBON MONOXIDE.

Formula, CO. Molecular Weight, 28.

Preparation. (1) Carbon Monoxide is formed when a stream of Carbon Dioxide is caused to pass slowly through a tube containing red-hot Charcoal or molten Zinc. It is necessary to pass the evolved gas through a wash bottle containing Caustic Soda in order to get rid of any Carbon Dioxide which may have escaped reduction :



If Oxygen or air is passed, slowly, through a tube containing red-hot Charcoal, Carbon Dioxide is first formed in the first portion of the tube, but is reduced to the Monoxide by the red-hot Charcoal in the second portion.

A similar series of reactions occurs in a Coke brazier. The reactions are easily followed from the accompanying diagram (Fig. 114). If the temperature at the top of the fire is not

hot enough to ignite the Carbon Monoxide, this poisonous gas escapes into the air. As a rule, the choking fumes evolved from these fires consist mainly of Carbon Dioxide.

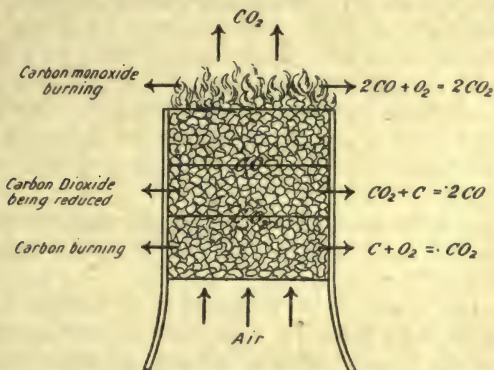


FIG. 114.—Chemical actions in a coke fire.

(2) Carbon Monoxide is most readily prepared, in the laboratory, by heating a mixture of Oxalic and Sulphuric

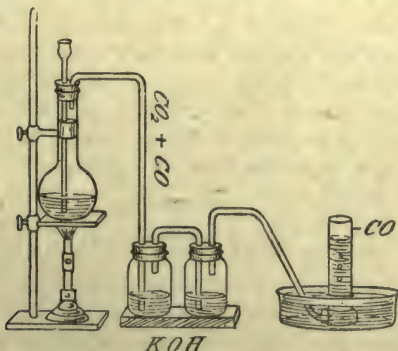
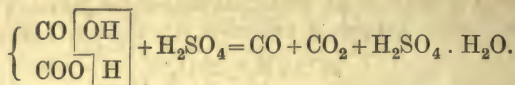


FIG. 115.—Preparation of Carbon Monoxide.

acids in a flask (Fig. 115). The Sulphuric acid takes the elements of water from the Oxalic acid, leaving a

mixture of Carbon Monoxide and Carbon Dioxide in equal volumes :

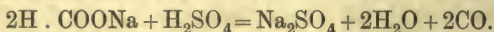


Most of the Carbon Dioxide can be extracted from the gaseous mixture by passing it through two wash bottles containing Caustic Potash, and the resultant gas can be collected over water.

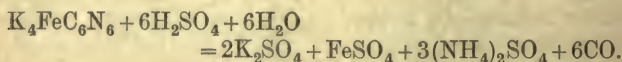
(3) If pure Carbon Monoxide is required, it can be obtained by gently warming a mixture of Sulphuric acid and Formic acid or a Formate. The action is similar to the one with Oxalic acid :



With Sodium Formate the equation is



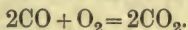
(4) Carbon Monoxide gas is also evolved when one part (by weight) of Potassium Ferrocyanide and a little water are mixed with ten parts of strong Sulphuric acid in a large flask :



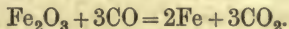
Properties. Carbon Monoxide is a colourless gas, and has no smell. This latter property makes it dangerous, as it is highly poisonous, and an escape is not readily detected. It acts upon the red corpuscles (haemoglobin) of the human blood, forming a bright cherry-red coloured compound, and preventing it from performing its functions of oxidizing waste tissue. Less than 1 per cent. in the atmosphere is sufficient to cause death. The gas may be formed when a coal-gas flame plays on a cold surface, as in a "water heater" in a badly ventilated bathroom, or in slow combustion stoves and charcoal braziers. Also it is now supplied, as "water gas" (p. 337), by many gas companies, in the public mains, making a leakage very dangerous.

Carbon Monoxide is nearly insoluble in water; 100 c.c. of water dissolve 3 c.c. of the gas at 5° C.

It burns quietly in air with pale blue flame, forming Carbon Dioxide; with Oxygen, it explodes, if a light is applied:



On account of its capacity for taking up an extra atom of Oxygen, Carbon Monoxide is a powerful "reducing agent." This fact is made use of in many metallurgical operations, *e.g.* the reduction of Ferric Oxide to metallic Iron in a blast furnace:



Carbon Monoxide is absorbed at ordinary temperatures by a solution of Cuprous Chloride in Ammonia. This property is made use of in separating (and determining the quantity of) the gas in mixtures with other gases.

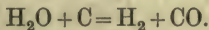
Composition. If a mixture of Carbon Monoxide with excess of Oxygen is exploded in a eudiometer tube and the volume of the Carbon Dioxide formed is ascertained by absorption with Caustic Potash, it is found that 2 volumes of Carbon Monoxide unite with 1 volume of Oxygen to produce 2 volumes of Carbon Dioxide.

Hence, by Avogadro's Law, 1 molecule of Carbon Monoxide with the addition of $\frac{1}{2}$ molecule, *i.e.* 1 atom, of Oxygen, produces 1 molecule of Carbon Dioxide.

That is: $x + \text{O} = \text{CO}_2$. Hence x must = CO.

WATER GAS.

When steam is passed over red hot Coke, the two react, forming a mixture of Hydrogen and Carbon Monoxide in equal parts:



Such a mixture has a high calorific power, and is of great value for heating purposes, but, as both constituents burn with non-luminous flames, it is of no value as an illuminant.

In places such as London, where there is no market for the large quantities of Coke produced at gas works, the Coke is used

to make water gas. The Coke is contained in large vertical cylinders lined with fire-brick. Air is passed through till the whole mass is almost white hot, then the air current is stopped and steam is turned in till the coke has cooled to a dull red heat, when the process is repeated. The resultant "water gas" is led into another cylinder, where a fine spray of crude petroleum is introduced to give illuminating power to the gas. It is then cooled and conducted to the gasometer, where it is mixed with the coal gas. The London Gas Light and Coke Company, at one time, supplied nearly 50 per cent. of water gas in the mains.

PRODUCER GAS.

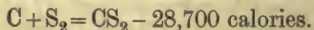
When air is blown through a large mass of red-hot Coke contained in a closed-in stove, the resulting gas is a mixture of Carbon Monoxide and Nitrogen. This mixture is called "Producer Gas," and can be led away in pipes, and, when burnt from proper burners, forms a very convenient form of fuel.

CARBON DISULPHIDE.

Formula, CS_2 . Molecular Weight, 76.12.

Preparation. Carbon Disulphide is formed by passing Sulphur vapour over red-hot Charcoal and condensing the resultant product in vessels surrounded by cold water.

The reaction is an endo-thermic one, *i.e.* heat has to be applied to make the two elements combine :

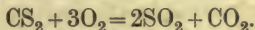


Properties. Pure Carbon Disulphide is a colourless, mobile liquid, with a not unpleasant aromatic smell, though the impure commercial liquid has a most disagreeable and rancid smell. It has a very high refractive index. It is heavier than water (Sp. Gr. 1.29), in which liquid it is practically insoluble.

Carbon Disulphide is a good solvent for many substances which are insoluble in water, *e.g.* Sulphur, Phosphorus, Iodine,

Gums, Resins, Fats and Caoutchouc, and is largely employed in industries on account of this solvent property.

It has a very low ignition point; a hot glass rod will set it alight, and it burns in air with a pale-blue flame. A mixture of Carbon Disulphide vapour with three times its volume of Oxygen explodes violently when a light is applied, forming the Dioxides of Sulphur and Carbon:



On account of its ready inflammability, a bottle of Carbon Disulphide should never be brought near a flame.

PROBLEMS.

59. Calculate the weight of Air (containing 23 per cent. of Oxygen) required to burn 5 grams of Coal containing 88.42 per cent. of Carbon, 5.61 per cent. of Hydrogen and 5.97 per cent. of Oxygen.

60. 32 c.c. of a gaseous Hydrocarbon require 112 c.c. of Oxygen for complete combustion, and produce 64 c.c. of Carbon Dioxide. Find a formula for the Hydrocarbon.

61. 3.4 c.c. of a Hydrocarbon are mixed with 22 c.c. of Oxygen and the mixture is exploded. The remaining gas after explosion measures 15.2 c.c., of which 13.6 c.c. is absorbed by Caustic Potash and the rest by Pyrogallic acid. Find the formula of the Hydrocarbon.

(Camb. Univ. Schol. Exam.)

62. 18 c.c. of a gas was mixed with 18 c.c. of Oxygen and the mixture exploded. The volume contracted to 15 c.c., and a further contraction of 6 c.c. took place when Caustic Potash was added. The remaining 9 c.c. were all absorbed by Pyrogallic acid. The vapour density of the gas was 5.33, and none of it was capable of absorption by Caustic Potash before exploding. What is the probable composition of the gas?

(Camb. Univ. Schol. Exam.)

63. The vapour of an organic compound containing Carbon, Hydrogen and Oxygen was mixed with Oxygen and exploded, being kept in a eudiometer at a temperature above 100°C . The following readings were made: 5.4 c.c. of the vapour with 32.4 c.c. of Oxygen produced 21.6 c.c. of Carbon Dioxide and 27 c.c. of Steam. All readings are at the same temperature and pressure. Find a formula for the substance.

(Camb. Univ. Schol. Exam.)

64. The gas in a vessel had the following gravimetric composition: 3.23 per cent. of Hydrogen, 19.35 per cent. Carbon and 77.42 per cent. Oxygen. It was approximately 13 times heavier than Hydrogen. What is the probable nature of the gas and its composition?

(Camb. Univ. Schol. Exam.)

65. A mixture of 5 c.c. of Hydrogen, 25 c.c. of Marsh Gas, 30 c.c. of Carbon Monoxide and 500 c.c. of Air (containing 21 per cent. of Oxygen) is exploded. What is left?

66. .5016 gram of a Carbonate is heated till all the Carbon Dioxide is driven off. The loss of weight is .176 gram. Find the percentage of Carbon in the Carbonate.

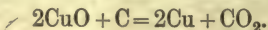
67. A litre flask containing a mixture of Carbon Dioxide, Oxygen and Nitrogen at 0° C. and 760 mm. was shaken up with Lime Water. The precipitated chalk was found to weigh .66 gram. Find the percentage of Carbon Dioxide in the flask.

68. One gram of Carbon Disulphide is completely burnt. Calculate the volume of Oxygen needed and the volumes of the gases produced, all volumes to be measured at 0° C. and 760 mm.

(Camb. Univ. Schol. Exam.)

PRACTICAL EXERCISES.

To show the Reducing Action of Charcoal. Make a mixture of powdered Copper Oxide and powdered Charcoal, using excess of the Charcoal. Place the mixture in a hard-glass test tube and heat strongly with a blowpipe. Allow the contents to cool in the test tube and then shake them out on to a piece of paper. The red particles of metallic Copper can be readily recognised among the black powder.



To shew the Bleaching Action of Charcoal. Warm a solution of Indigo or of Litmus with animal Charcoal for ten minutes. Filter and note the colourless nature of the filtrate.

To prepare Marsh Gas. Prepare a small quantity of Marsh Gas by the method indicated on page 315. Allow a jar full of the gas to burn (as a rule, the flame is luminous on account of impurities), and test the products of combustion with Lime water to prove the presence of Carbon Dioxide.

To prepare Olefiant Gas. Use the apparatus and substances indicated on page 319. Burn some of the gas, and prove that Carbon Dioxide is a product of its combustion. Disconnect the Caustic Potash washer, and prove the presence of Sulphur Dioxide in the unwashed gas.

To prepare Acetylene. Sink a crucible in a pneumatic

trough full of water, drop in a small lump of Calcium Carbide, and place over the crucible a jar full of water to collect the Acetylene. Burn a jar of the gas, and note the black smuts of Carbon produced by partial combustion.

To burn Acetylene fully, the apparatus in Fig. 106 must be used with a proper Acetylene burner.

To prepare Alcohol and Carbon Dioxide from Sugar. Place about 10 grams of Grape Sugar in a flask, dissolve it in water and add a few grams of Yeast. Fit on to the flask a single delivery tube, dipping into a beaker containing Lime water. Leave for 24 hours. Slow effervescence ensues when fermentation begins, the Lime water is turned milky, shewing that Carbon Dioxide is evolved, and Alcohol may be obtained from the liquid in the flask by fractional distillation (p. 5).

To find the percentage of Carbon Dioxide in a Carbonate. Set up an apparatus as in Fig. 116.

Weigh about 1 gram of the Carbonate into the small test tube. Place the tube in the flask as in the figure, and weigh the whole apparatus. Tilt the flask to allow action to take place between the Hydrochloric acid and the Carbonate, and continue to agitate its contents till all the solid is dissolved.

Warm the flask gently on a sand bath to expel any Carbon Dioxide which may be dissolved in the acid.

Fit a short piece of rubber tubing to *A*, take out the small piece of glass rod, and suck out, through the rubber tube at *A*, all the Carbon Dioxide left in the flask. Then replace the glass rod, take away the rubber tubing and weigh the whole apparatus.

The loss of weight gives the weight of Carbon Dioxide in the original weight of Carbonate taken; hence the percentage can be readily calculated.

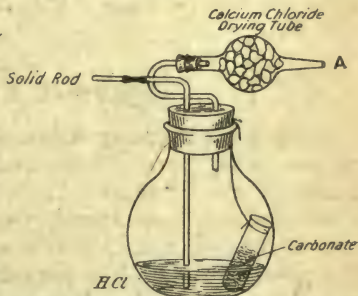


FIG. 116.—The percentage of Carbon Dioxide in a Carbonate.

To find the weight of a Litre of Carbon Dioxide. Fit up apparatus as in the diagram, taking care to see that all joints are gas-tight.

The small tube contains about a gram of powdered marble, and the flask contains dilute Hydrochloric acid. Before starting the action by allowing the acid to come in contact with the marble, weigh the whole apparatus below the rubber joint *R*. Now connect *R*, and tilt the flask till the action begins. Carbon Dioxide is given off, and is dried by the Calcium Chloride; it displaces the water in the aspirator, but

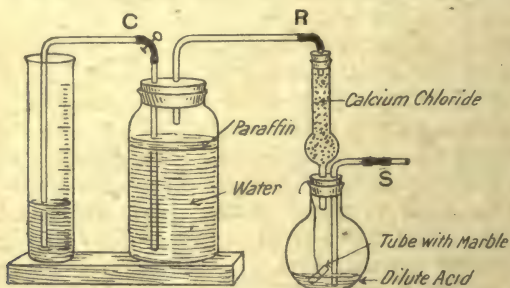


FIG. 117.—Weight of a Litre of Carbon Dioxide.

is prevented from dissolving in it by the layer of Paraffin. When all action has ceased, close the clip *C*, and let the water in the tube to the left of *C* run into the graduated cylinder. Read the volume of water in the cylinder. Disconnect *R*, open the stopper *S*, and suck out, through *R*, the gas left in the flask and tubes.

Weigh as before. The loss of weight represents the weight of Carbon Dioxide given off, and the volume of this gas at the temperature of the water is given by the volume of water which has been driven out into the cylinder. Correct this volume for temperature and pressure, and hence calculate the weight of 1000 c.c. of Carbon Dioxide at standard temperature and pressure.

A good result would be near 1.98 grams.

CHAPTER XXV.

COMBUSTION AND FLAME.

COMBUSTION is the term applied to any chemical process attended by the evolution of Light and Heat; the Light is caused by the phenomenon called a Flame, but this is by no means always present. The combustion of a hay stack is very evident when it is aflame, but it has none the less gone through the same chemical process when it has slowly rotted away; the same products of combustion are formed, and exactly the same number of units of heat are evolved, though, being spread over a much greater interval of time, it is not so apparent. Such a combustion is called Slow, and the one accompanied by flame is termed a Quick combustion.

Phlogistic Theory. Plato's assumption about combustion was, that all combustible bodies contained a common element which enabled them to burn; this was for a long time considered to be Sulphur, till Becher (1670) pointed out that many combustible substances contained no Sulphur.

Stahl (1723) gave to this hypothetical element the name Phlogiston, and this was supposed to rush out in the flame when the substances burned.

Metals were adjudged to be compounds of their Calces (Oxides) and Phlogiston; when the Phlogiston escaped the Calx was left. On this account Carbon was thought to be nearly pure Phlogiston, because the Calces of many metals when heated with Carbon apparently absorbed it and reproduced the metal.

The Phlogistic theory was definitely exploded by Lavoisier (1774), who shewed that metals *increased* in weight during calcination, and, at the same time, absorbed Oxygen from the air. Later, he discovered that the Diamond and Charcoal united with Oxygen when burning, to form Carbon Dioxide, and also that, when organic substances burned, they took Oxygen from the air to form Carbon Dioxide and Water.

Hence, he propounded the theory that Oxygen is necessary for combustion, and is absorbed during the process.

It is now known that other substances, such as Chlorine and Fluorine, can cause combustion, even if Oxygen is rigidly excluded, so that Lavoisier's conclusions, though accurate in the main, are not true for all cases.

Ignition Point. For every combustible substance there is a definite temperature to which it must be raised in air before combustion will take place; this temperature is called the Ignition Point. It varies greatly for different substances; Phosphorus, for instance, ignites at 60° C., a hot glass rod at a temperature of 120° C. will inflame the vapour of Carbon Disulphide, while the Diamond has to be heated to a white heat before it inflames.

It is not necessary, as a rule, to raise the whole of the combustible substance to this temperature, for, when combustion is once started, the heat evolved by the combustion of one particle will raise those near it to ignition temperature and cause them to inflame; one small spark will explode a whole barrel of gunpowder, and in this case the conduction of the combustion through the mass is extremely rapid.

Finely-divided Phosphorus will inflame spontaneously at ordinary temperatures, because the heat of the combination between it and the Oxygen of the air, is not conducted away sufficiently rapidly to prevent the Phosphorus being raised to its ignition point.

On the other hand, if a substance already burning well, such as a candle, is cooled below its ignition temperature, by placing a small spiral of Copper wire round the flame, it is extinguished. Again, if a square of gauze made of Copper wire is pressed over a bunsen flame, the flame does not penetrate the gauze,

though the presence of the gas above the gauze may be demonstrated by applying a lighted taper to it; similarly the gas

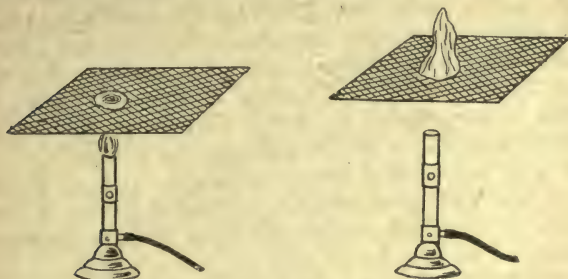


FIG. 118.—Effect of wire gauze on Flame.

can be lighted above the gauze without causing its ignition below (Fig. 118).

This non-conduction of flame, as it may be called, by wire gauze, was made use of by Sir Humphrey Davy (1815) in the construction of the miner's safety lamp; this consisted of an ordinary oil lamp with its flame completely surrounded by a cylinder of wire gauze. The fiery mine gases burnt within the cylinder of gauze, but, unless the gauze became red hot, did not inflame outside.

The ignition temperature of oils has a most important bearing where petroleum oils are used, either for lighting purposes or in internal combustion engines. The commercial term for it, in this connection, is Flash-Point, and it is defined as the temperature at which the oil gives off sufficient vapour to cause a small explosion when a flame is brought near its surface.

This temperature is determined by placing some of the oil in a metal tin suspended in a water bath (Fig. 119), warming

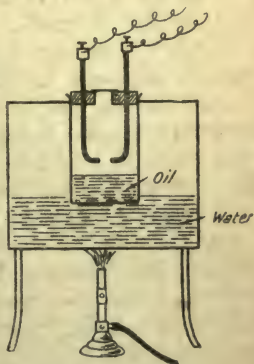


FIG. 119.—Flash Point.

the water, and sending, at intervals, a spark across the gap between the two metal terminals; when an explosion takes place, the small plate covering the circular hole in the cork is lifted by it, and the temperature at which this takes place is read on a thermometer (not shewn in the diagram).

The danger of using "low flash" oil in a paraffin lamp, especially if the reservoir is made of metal, is very great, as heat is transferred by conduction and radiation to the reservoir, and, as soon as the temperature is raised to the flash-point, the lighted wick is quite sufficient to cause an explosion with disastrous results. For this reason, it has been necessary to legislate against the use of kerosene or paraffin oil with a flash-point below a certain temperature; this is about 44°C. , but varies in different countries.

The smoother running of a petrol motor in summer than in winter, or when it has been running for some time and is warmed up, is due, to some extent, to the fact that the higher temperature vaporizes the petrol more readily and brings it well above its flash-point.

The Combustible and the Supporter of Combustion. Though it is convenient to speak of the burning substance as the combustible, and the surrounding gas, be it Air, Oxygen or what not, as the supporter of combustion, it must not be forgotten that combustion is really the chemical union of these two substances, and that, therefore, they are quite interchangeable.

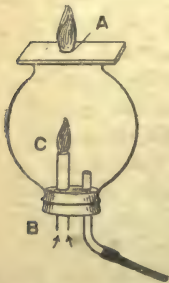


FIG. 120.—Inverted Combustion.

For instance, air will burn in an atmosphere of coal gas just as readily as coal gas will burn in air. If a glass globe (Fig. 120) has one end filled with a cork through which pass two tubes, one to admit air and the other coal gas, and the other end covered with a square of asbestos board having a small circular hole *A* cut in it; then, by covering the hole *A* with the thumb and allowing gas to pass in for a minute or so, the gas can be lighted as it issues at the point *B*, and, on removing the thumb and at the same time lighting the

gas at *A*, the flame at *B* passes into the globe, and there are now two flames, that at *A* being coal gas burning in air, and that at *C* being air burning in coal gas; this latter is often spoken of as inverted combustion.

In a similar manner Oxygen can be made to burn in the vapour of some inflammable liquid, such as Ether, by boiling the liquid in a flask (Fig. 121), igniting the vapour as it issues from the neck, and lowering a jet of Oxygen into the flask. This ignites in the flame at the neck of the flask and continues burning in the Ether vapour when lowered into it.

Flame. When both the substances taking part in combustion are gases or vapours—the phenomenon of flame is developed; if one of them is a solid, which is not vaporized at the temperature of its combustion—no flame appears.

Iron burning in Oxygen gives no perceptible flame, the bright light emitted being due to incandescent solid; on the other hand, Phosphorus, Sulphur, Wax, etc., burn with a flame because these solids are vaporized at the temperature of their combustion.

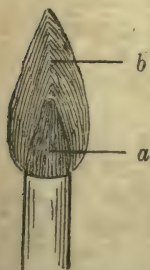


FIG. 122.—A single mantled flame.

The flames of most combustible gases are quite characteristic and recognizable: Sulphur burns in air with a pale lavender flame with a purple edge; the flame of Hydrogen gas in air is almost invisible in daylight, if the air is free from dust; Cyanogen has a most characteristic flame of peach blossom hue, while that of most of the Hydrocarbons has a yellowish white appearance.

The Structure of Flames. The simplest kind of flame is that produced by the direct union of two substances which undergo no decomposition, and form only one product of combustion in one single operation. Such flames are those of Hydrogen or Carbon Monoxide burning

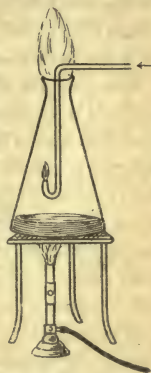


FIG. 121.—Combustion of Oxygen in Ether Vapour.

in air and Ammonia in Oxygen; they consist (Fig. 122) of a single hollow sheath of burning gas; the part *a* is nothing but unburnt gas, while the hollow sheath is represented by the area *b*. Such a flame is called a *single-mantled* flame.

That all flames contain a hollow cool centre of unburnt gases may be shewn in many ways. If the stick of an unstruck match is threaded with a pin about 2 cm. from the head and then the pin is placed cross-wise on the orifice of a bunsen burner; when the gas is turned on and lighted, the match head will not inflame for a considerable time, if at all.

If a small funnel (Fig. 123), 5 cm. in diameter, is covered with Copper wire gauze of fine mesh and connected to the gas

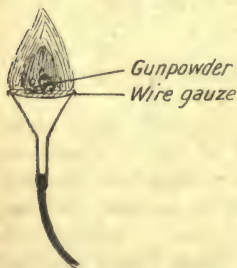


FIG. 123.—To prove that a flame is hollow.

supply, and then a small heap of gunpowder is placed at the centre of the gauze, the gas can be lighted without setting fire to the gunpowder, if the operation is performed carefully.

That this cool central portion consists of unburnt gas can be demonstrated by placing in it one end of a short glass tube; the gas rises through this, and can be ignited at its upper end. This experiment can be done with any kind of flame.

The majority of flames have not quite such a simple construction as the single-mantled flame of Hydrogen; they consist mainly of two conical sheaths, one inside the other, and are termed *double-mantled* flames.

Good examples of this type of flame are those of a candle (Fig. 124) and of coal gas (Fig. 125) burning in air. These flames consist of four parts :

- (1) A blue zone near the base.
- (2) A colourless zone of unburnt gas.
- (3) A bright luminous zone, made as large as possible by differently-shaped burners when the flame is required for illuminating purposes.
- (4) An exterior very faintly luminous mantle.

It has been proved that, in the blue portion at the base of the flame, the first stage in the oxidation of the Hydrocarbon takes place, the Carbon being changed mainly into Carbon Monoxide and the Hydrogen liberated mainly as such, though in part oxidized to Steam.

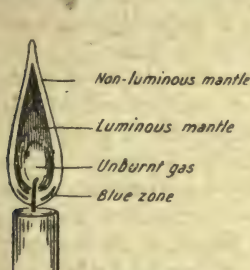


FIG. 124.—A candle flame.

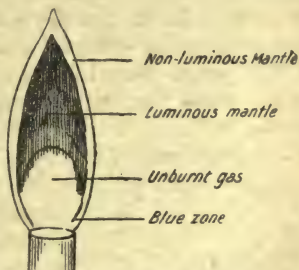
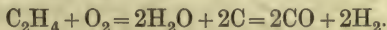
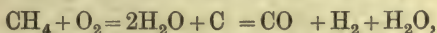


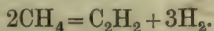
FIG. 125.—A coal gas flame.

These chemical changes are most probably brought about by the preliminary complete oxidation of the Hydrogen to Steam and the setting free of the Carbon; these two products at the high temperature of the combustion interact, forming Carbon Monoxide and free Hydrogen. These reactions are represented by the following equations, where Marsh gas and Ethylene are taken as typical Hydrocarbons :



Higher up the flame, in the non-luminous mantle, the Carbon Monoxide and Hydrogen burn, forming Carbon Dioxide and steam respectively.

The chemical changes which go on in the luminous portion of the flame are a matter of considerable doubt; the presence of Acetylene has been demonstrated in this region, and it may have been produced by the action of the great heat of the non-luminous mantle upon the undecomposed Hydrocarbons in the central portion, as thus :



Denser Hydrocarbons are in their turn formed from the Acetylene, until eventually Carbon itself is set free and raised to incandescence at the high temperature of the flame.

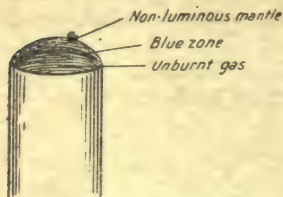


FIG. 126.—A very small coal gas flame.

It is by no means essential that Carbon itself should be liberated in a flame, in order that it should become luminous; for, dense Hydrocarbon vapours, when raised to a high temperature, become glowing and emit light on their own account.

The Acetylene produced in a gas flame can be rendered very evident by allowing the gas in a bunsen burner to burn at the gas orifice at the bottom of the metal tube; if, then, the gas evolved at the top of the tube is collected, it gives the characteristic reactions of Acetylene.

Again, since the Acetylene is formed in the inner cone of a coal-gas-air flame, it will be formed in the outer mantle when the flame is turned inside out by burning air in coal gas (Fig. 120), so that, in this flame, a considerable quantity of the Acetylene escapes combustion and can readily be detected in the coal gas which escapes.

If the supply of gas to a flame is very much diminished, or if air is admitted with the gas to the interior of the flame as in a bunsen burner, the luminous area becomes smaller and smaller (Figs. 126 and 127), and finally disappears altogether; the blue zone expands enormously in size and the outer non-luminous mantle becomes larger also and faintly luminous.

The greater heat of a bunsen flame, compared with that of

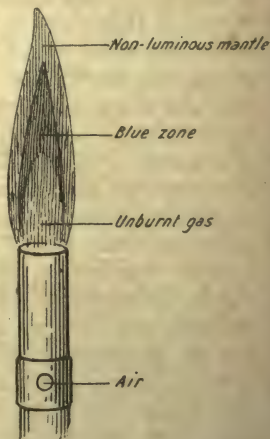


FIG. 127.—The flame of a bunsen burner.

a luminous coal-gas flame, is caused by the contraction in size in the area of the flame. The same number of heat units are evolved for the same quantity of gas supplied, but their evolution is concentrated in a much smaller space, which is thereby made considerably hotter.

The temperature of a bunsen flame, burning 6 cubic feet of coal gas per hour, has been determined, as to its various parts, as follows :

Tip of Inner cone	-	-	-	-	1090°
Centre of Outer cone	-	-	-	-	1533°
Tip of Outer cone	-	-	-	-	1175°

Smithell's Flame Separator. The presence of the two mantles in a bunsen flame is well shewn by means of an apparatus designed by A. Smithells (1891).

It consists of two coaxial glass tubes *A* and *B* (Fig. 128), which slide one within the other with a small amount of packing at *C*; the upper end of the tube *B* has an Aluminium nozzle fixed on to it, and the upper end of *A* a nozzle of Mica. The tube *B* is fixed over the top of a bunsen burner with some packing or a small cork; the upper ends of both *A* and *B* are brought together by sliding *A* downwards, the air-holes of the burner are stopped, and the gas ignited at the top of *A*, where it burns with a luminous flame. Air is now admitted, the flame becoming non-luminous, and then by sliding *A* carefully upwards, the two mantles are seen to separate, the outer one appearing on the tube *A* and the inner one on the tube *B*.

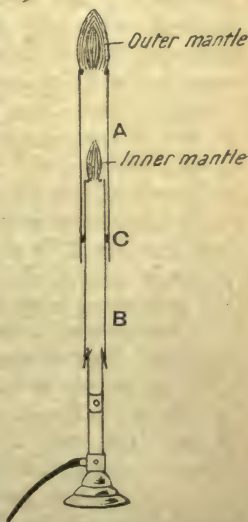


FIG. 128.—Smithell's Flame Separator.

By "tapping" the gases in the space between the two flames, they are found to consist mainly of Carbon Monoxide

and Hydrogen, which, as stated above, are the preliminary products in the combustion of coal gas.

Causes of Luminosity. A general explanation of the luminosity of all flames is not known; it was asserted by Sir Humphrey Davy (1815) that, whenever a flame is luminous,

solid particles, raised to incandescence, are always present in it, but this theory has been proved to be untrue in very many cases.

For instance, the flames of burning Phosphorus, of Phosphoretted Hydrogen and of Carbon Disulphide, when burnt in Oxygen gas, are brightly luminous, but contain no solid particles whatever.

The presence of solid particles in a flame is shewn by Soret's optical test, in which a strong light is projected on to a flame and then on to a screen; when solid par-

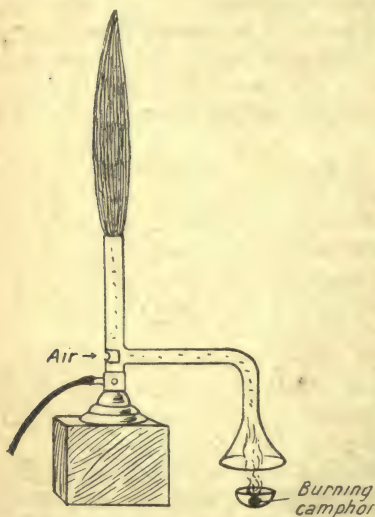


FIG. 129.—Solid particles in a bunsen flame.

ticles are present, as in a candle flame, a shadow is cast upon the screen, but the above-mentioned flames throw no shadow.

That a non-luminous flame is made luminous by the introduction of solid particles into it, may be shewn by allowing the Carbon particles in the smoke arising from burning Camphor to pass in at one of the air-holes of a bunsen burner (Fig. 120), the flame of which immediately becomes luminous.

The artificial introduction of solid matter into a non-luminous flame in order to produce luminosity is instanced in the Welsbach incandescent mantles; these are made of an earth consisting of Thorium Oxide with 1 per cent. of Cerium Oxide, and, when they are placed over an ordinary bunsen

flame, they are raised to incandescence and emit a bright light.

As has already been seen (p. 337), the non-luminous Carbon Monoxide and Hydrogen flame of Water gas is made luminous by the introduction into the gas, before burning, of a small percentage of dense Hydrocarbon vapours.

The influence of pressure upon the luminosity of a flame is considerable, and a jet of Hydrogen burning in Oxygen at a pressure of two atmospheres becomes sufficiently luminous to give a continuous spectrum when examined by the spectroscope.

The temperature, also, of the burning gases has a very important effect on the luminosity of the flame; the higher the temperature the greater the light emitted. This effect is noticed when a candle burns in Oxygen, instead of air; the effect of the Oxygen is to increase the temperature of the flame very considerably, and a light, which rivals that of Acetylene, is produced.

Also, if the gas supplied to an ordinary coal-gas burner has its temperature raised by heating the tube along which it is passing to feed the burner, the candle power of the flame produced is greatly increased.

To sum up, Luminosity is due to two main causes: (1) The presence in the flame of solid particles rendered incandescent, either by the heat of the flame gases or their own combustion. (2) The presence in the flame of vapours sufficiently dense to become self-luminous at the temperature of the flame. The luminosity of a candle flame, and that of Hydrocarbons in general, is most probably due to both these effects being produced simultaneously.

Spontaneous Combustion. Cases of spontaneous combustion are practically all of them due to the union of the combustible substance with the Oxygen in the air, in such a confined space that the heat of combination is not dissipated quickly, so that, eventually, the whole mass may take fire and be consumed.

This action takes place in hay stacks when the hay has been packed before it is sufficiently dry; in coal bunkers, where the primary cause is the oxidation of the Iron Pyrites

contained in the coal; and also in heaps of greasy rags containing an oil, such as linseed, which takes up Oxygen from the air in the ordinary way and becomes dry, a certain amount of heat being evolved in the process.

Pyrophoric powders may be made of finely-divided Lead by carefully heating Lead Tartrate in a glass tube, having only a small aperture, and sealing up this aperture when decomposition is complete; on breaking open the tube and shaking the contents out into the air, the finely divided Lead takes fire, causing a cascade of sparks.

PRACTICAL EXERCISES.

Experiments on Ignition Temperatures. (1) Dissolve a very small piece of yellow Phosphorus in about 1 c.c. of Carbon Disulphide. Place two or three drops of this solution on a piece of filter paper. As the solvent evaporates, it leaves Phosphorus in such a finely-divided condition on the filter paper that it takes fire at ordinary room temperature.

(2) Place two or three c.c. of Carbon Disulphide in a porcelain dish. Warm a glass rod in the flame, and dip it into the liquid. Long before the rod is red hot, it will be found to ignite the Carbon Disulphide.

(3) Perform a similar experiment to the last with Alcohol. Use an Iron rod, and note that it has to be made almost white hot in a blowpipe flame before it ignites the Alcohol.

To determine the Flash-Points of Paraffin and Colza Oils. Place about 20 c.c. of the oil in a porcelain dish with a thermometer and a stirrer. Place the dish and its contents over a *small* bunsen flame, and warm the oil very gradually with constant stirring. Every two degrees rise of temperature above 40° C., apply a lighted match *near* the surface of the oil. When the temperature reaches the flash-point the vapour above the oil will take fire. Observe the temperature when it first takes fire.

Put out the lighted oil, take away the bunsen burner and allow the oil to cool. Apply a light as before, and note the first temperature at which the oil does not catch fire.

A mean of these two temperatures gives the flash-point.

Paraffin oil will usually "flash" between 50°C . and 70°C ., but the flash-point of Colza oil is above 200°C ., and a long range thermometer must be used in its determination.

To separate the two Mantles of a Bunsen Flame. Set up Smithell's apparatus and perform the experiment described and illustrated on page 351.

To show the Spontaneous Combustion of Lead. Make some "Pyrophoric powder" by heating Lead Tartrate in a test tube, the mouth of which has been drawn out in the flame so as to have only a small aperture. Allow the finely-divided Lead to escape into the air.

CHAPTER XXVI.

SILICON, TIN AND LEAD.

If reference is made to the table of the Periodic System of Elements (p. 137), Carbon will be found at the head of Group IV., and below it, besides the unimportant and rare elements Titanium, Germanium, Zirconium, Cerium and Thallium, are found three important elements Silicon, Tin and Lead.

When the properties and compounds of the four elements Carbon, Silicon, Tin and Lead are studied, considerable similarity is noticed, and a gradual change from distinctly non-metallic Carbon to metallic Lead.

The common valency is 4, though all, except Silicon, are di-valent as well.

Tetra-valent compounds are the Hydrides of Carbon and Silicon, CH_4 and SiH_4 ; the Oxides, CO_2 , SiO_2 , SnO_2 and PbO_2 ; and the Chlorides, CCl_4 , SiCl_4 , SnCl_4 and PbCl_4 .

Di-valency is seen in the Oxides, CO , SnO , PbO , and the Chlorides, SnCl_2 and PbCl_2 .

The Dioxides of all four elements may be regarded as the Anhydrides of four similarly constituted acids: Carbonic, $\text{CO}(\text{OH})_2$, Silicic, $\text{SiO}(\text{OH})_2$, Stannic, $\text{SnO}(\text{OH})_2$, and Plumbic, $\text{PbO}(\text{OH})_2$. Many other points of similarity between the members of this group may be unearthed by a little study.

SILICON.

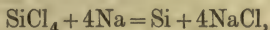
Symbol, Si. Atomic Weight, 28.3.

Occurrence. Silicon is not found free in nature, but, in combination, it is, next to Oxygen, the most abundant and

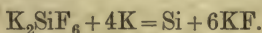
widely distributed of all the elements; about 27 per cent. of the earth's crust consisting of Silicon. This is because its Oxide, SiO_2 , occurs, in large masses as Sandstone and Quartzite, and combined with metallic Oxides as Silicates, the most abundant of which is Aluminium Silicate, which is the principal constituent of Clay.

Silicon can be obtained in two varieties: Amorphous and Crystalline; the former was first prepared by Berzelius in 1823 and the latter by Deville in 1854.

Preparation. Amorphous Silicon may be obtained by heating Sodium or Potassium in an atmosphere of Silicon Tetrachloride:



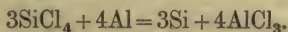
or by heating the Fluosilicate of Sodium or Potassium with the metal itself:



Quartz, SiO_2 , may be reduced to Silicon by mixing it with Magnesium powder and heating the mixture strongly:



Crystalline Silicon is made by passing the vapour of Silicon Tetrachloride over molten Aluminium:

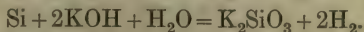


The Silicon dissolves in the molten metal and may be obtained by dissolving the Aluminium away with Hydrochloric acid.

Properties. Amorphous Silicon is a dark-brown powder. It melts at 1500°C ., but, when heated in air, a surface skin of the Dioxide, SiO_2 is formed, which protects it from further oxidation.

It is insoluble in all acids except Hydrofluoric.

When boiled with Caustic Potash it dissolves, forming Potassium Silicate and evolving Hydrogen gas:



Crystalline Silicon occurs as steel-grey needle-shaped crystals, which are hard enough to scratch glass. In its chemical properties, it resembles Amorphous Silicon, but it is not so active.

SILICON DIOXIDE OR SILICA.

Formula, SiO_2 . Molecular Weight, 60.3.

Occurrence. This compound is one of the most important of those in the earth's crust. Certain animals—Diatoms, Radiolaria and Sponges—make their skeletons of it, and large deposits of these skeletons are found in an earth called *Kieselguhr*.

Silica is found both in crystalline and amorphous states. *Quartz* or *Rock Crystal* consists of very pure Silica. It occurs in colourless transparent hexagonal crystals (Fig. 130), and in the massive state as the rock *Quartzite*.

The crystals are sometimes coloured with traces of various Oxides: Amethyst Quartz contains Oxide of Manganese, Smoky Quartz and Cairngorm contain traces of Carbonaceous matter, and Milky Quartz owes its opaque nature to numberless very tiny air bubbles.

Amorphous Silica is found in *Opals* and *Agates*, whilst *Flint*, *Calcedony* and *Jasper* consist mainly of this substance.



FIG. 130.—A crystal of Quartz.

Properties. Pure Silica is a colourless transparent solid, which has a sufficiently high refractive index to sparkle somewhat like a diamond when properly cut and polished. It is just hard enough to scratch glass.

It cannot be melted to a true liquid, but begins to soften at a temperature of 1600°C . It has such a very low coefficient of expansion ($\cdot 0000005$), that red-hot articles made of Silica can be plunged into cold water without cracking, whilst ordinary glass, under the same conditions, would burst into fragments. For this reason it is used for making crucibles, tubes and flasks which have to stand high temperatures without melting.

Silica is practically insoluble in water, and all acids except Hydrofluoric. It is, however, attacked by superheated water and by boiling solutions of the Caustic Alkalies and the

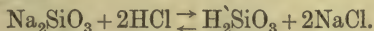
Alkaline Carbonates; hence its presence in the water of geysers.

Silica is an acidic Oxide and, at high temperatures, readily unites with basic Oxides to form salts called Silicates.

Silica, which has been softened by heat, can be drawn out into extremely thin threads or fibres, of great tensile strength for their size, and of perfect elasticity; they are used for suspending small mirrors, etc., in delicate electrical instruments.

Diatomaceous earth—called Tripoli or Kieselguhr—is used as a polishing powder, for cement and for dynamite.

Silicic Acid H_2SiO_3 . When a dilute solution of Sodium Silicate, Na_2SiO_3 is treated with dilute Hydrochloric acid, Silicic acid, H_2SiO_3 and Salt are formed, and the acid remains in the solution unless it is boiled, when a deposit of gelatinous Silica is thrown down:



The Silicic acid can be separated from the Salt and the excess of Hydrochloric acid by a process which is called "*Dialysis*."

This process depends, for its working, upon the fact that substances which are soluble in water can be divided into two classes, according as they will, or will not, pass through a parchment membrane. The former class are called "*Crystalloids*" and the latter "*Colloids*." Now both Hydrochloric acid and Salt are crystalloids, but Silicic acid is a colloid; consequently, if the solution formed by the above-mentioned reaction is placed in a parchment drum and floated on a basin of water (Fig. 131), the Salt and Hydrochloric acid molecules diffuse through into the water, and may be removed by changing the water once or twice, but the Silicic acid remains in the drum, and a dilute solution may thus be obtained.

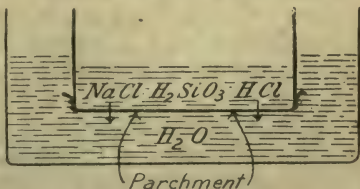


FIG. 131.—Dialysis of Silicic acid.

This dilute solution can be strengthened, to a concentration of 5 per cent., by careful evaporation in vacuo.

Silicic acid is a di-basic acid, and forms numerous salts called Silicates. All these salts are insoluble in water (and most acids) except the Silicates of Sodium and Potassium, which are usually called Water-glass. This substance is used for the preservation of eggs; it forms an insoluble, impermeable coating of Calcium Silicate round the egg, which prevents the entry of bacteria which would cause decay.

Glass. Glass is a complicated mixture of several Silicates, notably those of Sodium, Potassium, Calcium and Lead. It is made by fusing together in a furnace a mixture of white Sand, Limestone, Sodium or Potassium Carbonate, and Litharge or Red Lead in the proper proportions.

After the reactions have ceased, the glass is taken from the crucibles and moulded or blown into the required shapes by various methods. It is then allowed to cool slowly in an annealing oven, as rapidly cooled glass is liable to be very brittle and easily broken.

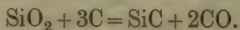
Ordinary *window glass and bottle glass* is a Soda-Lime Silicate; it is comparatively soft and fuses readily. The green colour is due to the presence of Iron in the Sand, and may be got rid of by adding a small quantity of Manganese Dioxide, which oxidizes the green Ferrous Silicate to pale yellow, practically colourless, Ferric Silicate.

Bohemian glass is a Potash-Lime Silicate; it is hard and melts at a high temperature. It is also less soluble in water than Soda glass.

Flint glass is a Lead-Potash Silicate; it is very lustrous when polished, and has a high refractive index. It is used for making lenses and for artificial gems—Parisian diamonds.

Glass is coloured by adding various metallic Oxides to the original mixture. It is made milk-white by the addition of bone ash.

Carborundum, Silicon Carbide SiC. This compound is made by fusing a mixture of Coke and white Sand in an electric furnace for about eight hours:



When pure it is colourless, but is often tinted by impurities. It is not attacked by any acid—even Hydrofluoric acid. It is nearly as hard as the diamond, and is used for making grinding wheels, whetstones and hones.

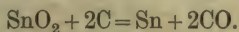
TIN.

Symbol, Sn. (Stannum). Atomic Weight, 119.0.

History. Tin has been found in Egyptian tombs, so that the knowledge of the metal dates back to very early times. The early Phoenicians used it, and Pliny says that Tin (*cassiteron* in Greek) is obtained from the Cassiterides, *i.e.* the British Isles, referring undoubtedly to the Cornish Tin mines, which are still working.

Occurrence. Practically the only ore of Tin of any commercial value is *Tinstone* or *Cassiterite*, SnO_2 . This ore is found in very few places, but in large deposits. The principal localities are the Malay peninsula and archipelago, Bolivia, Cornwall, Australia and South Africa. *Stream Tin* is a very pure form of Cassiterite found in nodules.

Preparation. The crushed ore is first subjected to the process of washing in a stream of water; its density (6.9) causes it to remain at the bottom when earthy matter is carried away by the stream. It is then roasted in a reverberatory furnace (Fig. 132) in a strong current of air, by which any Arsenic or Sulphur present is removed as Oxide, and afterwards, Anthracite Coal is added and the draught partially closed, when the Oxide is reduced to the metal:



The crude Tin thus obtained is refined by "*liquation*," *i.e.* melting it on a sloping hearth, whereby the easily melted Tin runs away down the slope, leaving most of the impurities behind. Afterwards the molten metal is stirred with a billet of wood, when the gases escaping from the wood carry impurities with them to the surface, where they collect as "*dross*," which is skimmed off. This process is called "*Poling*."

Properties. Tin is a bright white lustrous metal, which does not tarnish in air. It can be cut with a knife, but is harder than Lead, though softer than Zinc.

It is very malleable and ductile at ordinary temperatures, and can be beaten out into foil—Tinfoil—but at 200° C. it is so brittle that it can be powdered.

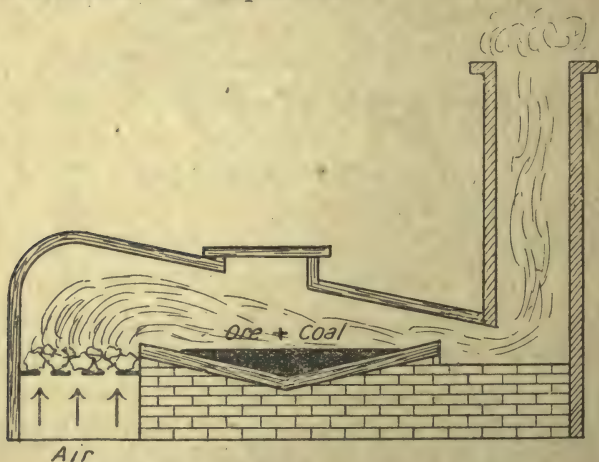
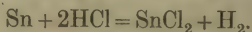


FIG. 132.—Diagrammatic section of a reverberatory furnace.

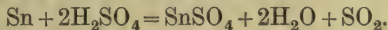
It melts at 228° C., and has a marked tendency to crystallize on solidification. Good crystals may be obtained by allowing it to solidify partially in a crucible and pouring away the molten part or by placing a little warm dilute aqua regia on the surface of a Tin block, when its crystalline nature becomes apparent at once.

When Tin is heated in air, just above its melting point, for some time, it becomes covered with a greyish white scum, which is Stannic Oxide, but, at a temperature of about 1500° C., Tin will take fire in air, burning with a bright flame.

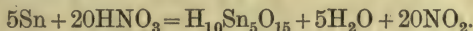
Tin dissolves slowly in dilute, and quickly in strong Hydrochloric acid, forming Stannous Chloride and liberating Hydrogen :



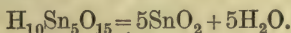
Cold concentrated Sulphuric acid has little action on the metal, but, if heat is applied, the Tin is dissolved with the formation of Stannous Sulphate and evolution of Sulphur Dioxide :



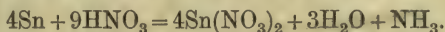
With concentrated Nitric acid, Tin forms a white insoluble powder, Metastannic acid :



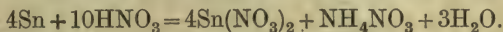
This substance, on heating, gives off water, leaving behind Stannic Oxide, SnO_2 :



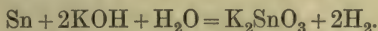
In cold dilute Nitric acid, Tin dissolves slowly, forming Stannous Nitrate and giving off Ammonia gas :



The Ammonia unites with a molecule of Nitric acid, forming Ammonium Nitrate, so the equation should be written :



Tin dissolves in boiling Caustic Alkalies, forming Stannates and giving off Hydrogen :



The fact that Tin is not affected in ordinary air is made use of in the manufacture of "Tin plate," which is merely Iron plate with a thin coating of Tin. The Iron plates are made thoroughly clean from Oxides, by dipping them in dilute Hydrochloric acid, and from grease by dipping in a solution of Alkali, and are then dipped in a bath of molten Tin.

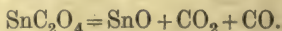
Many important alloys contain Tin. *Pewter* consists of three parts of Tin and one part of Lead; common *Solder* contains equal parts of Tin and Lead; and *Britannia metal* contains 84 parts Tin, 10 parts Antimony, 4 parts Copper and 2 parts Bismuth.

COMPOUNDS OF TIN.

Tin possesses two valencies, bi- and tetra-, and has two sets of compounds corresponding to the two valencies.

It has two Oxides, Stannous Oxide, SnO and Stannic Oxide, SnO_2 , and from them the two series of salts, Stannous and Stannic, are derived.

Stannous Oxide SnO is formed by heating Stannous Oxalate out of contact with air :



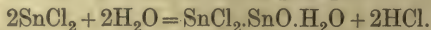
It is a black powder, which burns when heated in air, forming the Dioxide. It dissolves in acids, forming Stannous Salts.

Stannic Oxide SnO_2 is formed when Tin is heated in air or when Metastannic acid, the product of the action of strong Nitric acid on Tin, is heated.

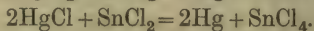
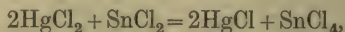
It is a white powder, which turns temporarily yellowish-brown on heating. It is unacted upon by acids, but with fused Caustic Potash yields Potassium Stannate, K_2SnO_3 .

Mixed with Turpentine or other drying oils, Stannic Oxide is used for "*putty*."

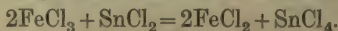
Stannous Chloride SnCl_2 is obtained by dissolving Tin in Hydrochloric acid and evaporating the solution. It can be prepared as white crystals $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, which dissolve in a small quantity of water, but, with excess of water, or on exposure to the air, a basic Chloride is precipitated :



Stannous Chloride is a powerful reducing agent, owing to the readiness with which it combines with either Oxygen or Chlorine. Thus Mercuric Chloride is first reduced by it to white Mercurous Chloride and afterwards to a grey precipitate of metallic Mercury :



It is used in the volumetric analysis of Iron compounds (p. 478) for reducing Ferric Chloride to Ferrous Chloride :



Stannic Chloride SnCl_4 is obtained by passing dry Chlorine gas over molten Tin, as indicated in the diagram (Fig. 133). It condenses as a colourless fuming liquid in the test tube. One of its Hydrates, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, is employed as a mordant for dyeing.

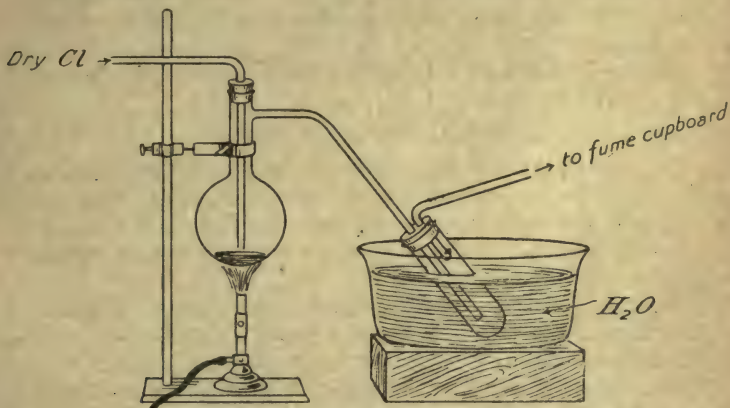


FIG. 133.—Preparation of Stannic Chloride.

Stannous Sulphide SnS is obtained as a dark grey mass when Tinfoil is introduced into Sulphur vapour.

When Sulphuretted Hydrogen gas is passed through a solution of Stannous Chloride, a brown precipitate of hydrated Stannous Sulphide is formed. This compound loses water, and becomes a dark grey powder on heating.

Stannic Sulphide SnS_2 is formed when Stannous Chloride, Sal-ammoniac and Sulphur are heated together. It is a golden-yellow crystalline substance, largely used as a pigment known as "mosaic gold."

Detection of Tin. Salts of Tin are recognized by the fact that they give brown or yellow precipitates with Sulphuretted Hydrogen, according as they are Stannous or Stannic salts; these precipitates are both soluble in hot Caustic Soda.

On Charcoal, with fusion mixture, a white malleable bead of Tin is obtained before the blowpipe.

When a little Hydrochloric acid is added to a Tin salt, together with a small piece of Zinc, a grey deposit of spongy Tin is formed on the Zinc.

LEAD.

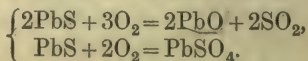
Symbol, Pb. (Plumbum). Atomic Weight, 207.1.

History. Lead was known to the ancient Egyptians; it is also mentioned in the Old Testament. It was confused at one time with Tin, and Pliny distinguishes between *Plumbum nigrum* (Lead) and *Plumbum album* or *candidum* (Tin). The ancient Romans used Lead for making water pipes.

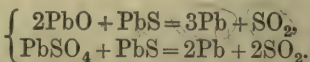
Occurrence. Lead is very occasionally found native in nature. Its principal ore is *Galena*, Lead Sulphide, PbS , which occurs in very large deposits. Other minerals containing Lead are *Cerussite*, Lead Carbonate, PbCO_3 ; *Anglesite*, Lead Sulphate, PbSO_4 ; *Crocosite*, Lead Chromate, PbCrO_4 ; and *Pyromorphite*, Lead Chloride and Phosphate, $\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{PO}_4)_2$. *Galena* is found and worked in many localities, amongst which are the famous Broken Hill mines in New South Wales, also in various parts of England, the United States, Germany and Mexico.

Preparation. Lead is extracted from *Galena* by two processes.

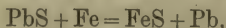
(1) The *Galena* is first roasted, *i.e.* heated in a strong current of air, in a reverberatory furnace (Fig. 132). This oxidizes the ore partly to Oxide and partly to Sulphate of Lead :



The draught is then partially shut off, more *Galena* is introduced, and further heating causes complete reduction to metallic Lead :



(2) In this process, advantage is taken of the fact that, at a high temperature, Iron will take the place of Lead in Lead Sulphide, thus :



The process is conducted in a blast furnace, and the Ferrous Sulphide rises to the top of the molten Lead and may be drawn off.

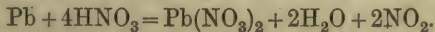
Lead obtained by either process usually contains impurities consisting of Antimony, Tin and Copper. These are removed by heating the metal in a shallow reverberatory furnace, when the impurities oxidize first and rise to the surface as "dross," which may be skimmed off. It still contains Silver, which is extracted by various processes (see Silver).

Properties. Lead is a soft bluish-grey metal, which has a bright metallic lustre when freshly cut. This lustre soon disappears in ordinary air, and the metal assumes its customary "lead" colour. This change does not occur in perfectly dry air or in air-free water; as with Iron, a mixture of the two is necessary.

Lead is so soft that it can be scratched with the finger-nail, and it leaves a grey streak when drawn across paper. Lead is not very tough, and cannot be hammered out into thin sheets like Gold, but it can be pressed into pipes or rolled into foil.

Lead has a density of about 11.3. Lead melts at 326°C. , and, in air, a thin dark grey film of Lead Suboxide, Pb_2O forms on its surface, but this, on further heating, changes to Litharge, Lead Monoxide, PbO . When cooled slowly, the molten metal solidifies in the form of crystals, which are octohedral in shape, and a similar crystalline "growth" of Lead is obtained by the electrolysis of any soluble Lead salt, or by hanging a strip of Zinc or Iron in a solution of Lead Acetate or Lead Nitrate.

Lead is at once attacked and dissolved by Nitric acid, forming Lead Nitrate and giving off red Nitric fumes:



Dilute Sulphuric or Hydrochloric acids do not attack Lead, because an insoluble crust of the Sulphate or Chloride of Lead is formed, which stops further action, but powdered Lead is dissolved by both these acids when they are concentrated and boiling.

Pure water will dissolve Lead to a certain extent, and, as all Lead salts (and Lead itself) are poisonous, this is a fact

that has to be taken into account when the water supplied for drinking purposes is very pure. In these cases the water is usually made to take up a small quantity of a Calcium salt, either the Carbonate or the Phosphate, before it is allowed to enter the leaden supply pipes, as the presence of these salts prevents its solvent action on the Lead. On the other hand, the presence of Ammonium salts, notably the Nitrate, or of Carbon Dioxide in any quantity, increases its solvent power.

On account of the ease with which Lead can be worked, bent, cut and soldered, and also of its power to resist the attacks of water and acids, it is very largely used in arts and manufactures. Some of its uses are for pipes, for sheathing electric cables, for cisterns and roofs and for chambers in the manufacture of Sulphuric acid. It is also used for making bullets. These are pressed into their moulds; not poured in molten and allowed to solidify, because Lead contracts on solidification, and this would leave a small cavity in the bullet which would render its flight untrue.

Lead is largely employed, nowadays, in the making of accumulator plates.

It enters into the composition of many important alloys; these have most of them been discussed under Tin (*q.v.*).

COMPOUNDS OF LEAD.

Lead forms five compounds with Oxygen: the Suboxide, Pb_2O , Monoxide, PbO , Sesquioxide, Pb_2O_3 , Red Lead, Pb_3O_4 , and Lead Peroxide, PbO_2 . Only three of these are of sufficient importance to be discussed here.

Lead Monoxide, Litharge or Massicot, PbO . This compound is formed when Lead is heated in air or in Oxygen, when any of the other Oxides are strongly heated and also by heating the Nitrate or Carbonate of Lead.

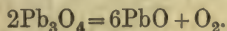
Lead Monoxide is a yellow powder, known commercially as *Massicot*, and, when melted and allowed to cool, it acquires a pinkish tinge and a crystalline nature, and is known as *Litharge*. It is very slightly soluble in water, 1 part in 7000,

and gives to the water a faintly alkaline reaction. It dissolves readily in most acids forming the different salts of Lead.

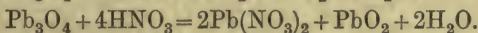
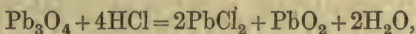
Large quantities of Litharge are used in preparing oils and varnishes, and for making flint glass.

Triplumbic Tetroxide, Red Lead or Minium, Pb_3O_4 . Red Lead is made by heating Litharge or Lead Carbonate in air for some time at a temperature of about $450^\circ C$.

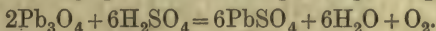
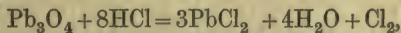
Red Lead is a scarlet powder; when heated it darkens in colour, becoming almost black, and eventually gives off one atom of Oxygen, leaving behind Litharge:



Though it is a true compound, it behaves towards dilute acids as if it were a mixture of Litharge and Lead Peroxide ($2PbO + PbO_2$), the Litharge acting as a basic Oxide and dissolving, forming a Lead salt, while the Lead Peroxide separates out:



With strong Hydrochloric or Sulphuric acids, the Peroxide is also acted upon, giving off Chlorine gas and Oxygen respectively:



Red Lead is used to a large extent by plumbers, also in the making of glass and pottery glaze and for paint.

Lead Peroxide PbO_2 . Lead Peroxide is most readily prepared by the action of dilute Nitric acid on Red Lead, when it is precipitated as a puce-coloured powder. It is also formed when Litharge, suspended in an alkaline solution, is subjected to the action of an oxidizing agent, such as Bleaching powder, Chlorine or Hydrogen Peroxide. The brown deposit formed on the anode when a Lead salt is electrolysed with Lead electrodes consists of Peroxide of Lead.

Lead Peroxide is a brown or puce-coloured powder. It is a strong oxidizing agent, as it parts with one atom of Oxygen

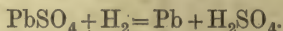
quite readily. If a mixture of this substance and Sulphur is gently rubbed in a mortar, the mass inflames. If a jet of Sulphuretted Hydrogen is caused to impinge on a little Lead Peroxide, the heat of the oxidation is sufficient to cause the gas to inflame. When strongly heated, Lead Peroxide evolves Oxygen, leaving behind Lead Monoxide.

Nitric acid has no action on this substance, but hot concentrated Hydrochloric and Sulphuric acids yield Chlorine and Oxygen respectively, just as with Red Lead.

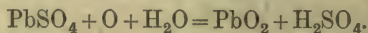
Lead Peroxide acts both as an acidic and a basic Oxide. When boiled with Caustic Potash, a compound Potassium Plumbate, K_2PbO_3 , similar to Potassium Stannate, K_2SnO_3 , is formed; here the Peroxide is acidic. With cold concentrated Hydrochloric acid, a yellow liquid is formed containing Lead Tetrachloride, $PbCl_4$; here the Peroxide is basic.

A salt in which Lead exhibits its tetra-valency is made by dissolving Red Lead in glacial Acetic acid. It consists of pale green crystals, and is called Lead Tetracetate, $Pb(C_2H_3O_2)_4$.

Accumulator Cells. If two Lead plates are covered with a paste of Litharge and immersed in a 20 per cent. solution of Sulphuric acid, the Litharge is converted into white Lead Sulphate, $PbSO_4$. If an electric current of about 1 ampère is now passed through the cell, the Hydrogen liberated at the kathode reduces the Lead Sulphate to spongy Lead, and Sulphuric acid is returned to the solution:

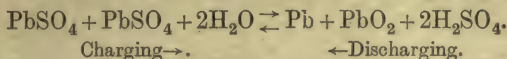


At the same time the Oxygen given off at the anode causes the formation of Lead Peroxide on the plate:



The cell is now in such a condition that, if the terminals are joined by a wire, a current having a pressure of two volts can be obtained from it, running, through the wire, from the Peroxide plate to the Lead plate, and, as the current flows, the reverse changes to those noted above occur, and, when both plates are covered with white Lead Sulphate, the current ceases.

The two actions may be represented thus :



An arrangement of this kind forms, therefore, a very simple way of storing electricity, and the current obtained from these accumulator cells is strong and steady.

Chlorides of Lead. Lead forms two compounds with Chlorine : Lead Dichloride, PbCl_2 and Lead Tetrachloride, PbCl_4 .

The formation of the latter from Lead Peroxide and cold concentrated Hydrochloric acid has been noted above. It is a yellow fuming liquid, which is not at all stable, and quickly dissociates in the presence of moisture into Lead Dichloride and Chlorine.

Lead Dichloride, PbCl_2 is formed as a white precipitate when Hydrochloric acid, or any soluble Chloride, is added to the solution of a Lead salt. The white powder is soluble in hot water, but separates out as crystals of Lead Chloride when the liquid cools. 100 grams of water dissolve 4 grams of Lead Chloride at 100°C ., but only .7 of a gram at 0°C . ; hence the precipitation on cooling.

Lead Nitrate $\text{Pb}(\text{NO}_3)_2$ is one of the few salts of Lead which are soluble in water. It is obtained by dissolving Litharge in Nitric acid.

Lead Carbonate PbCO_3 is obtained, as a white precipitate, when Sodium Bicarbonate, NaHCO_3 is added to a soluble salt of Lead. If normal Sodium Carbonate is used, the precipitate consists of basic Lead Carbonate $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$. This latter compound is known as "*White Lead*," and is largely used as the basis of most paints, owing to its great "covering" power.

White Lead is manufactured on the large scale by several processes, and the oldest and best of these is known as the Dutch method. In this process coils of sheet Lead or leaden gratings, made so as to have a large surface, are placed in pots (Fig. 134), the lower part of which contains a little Acetic acid or Vinegar. A hundred or more of these pots are stacked

in layers in a brick house with fermenting tan bark between

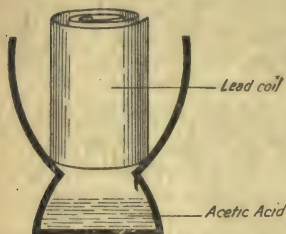


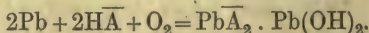
FIG. 134.—Preparation of White Lead.

each layer. In about ten or twelve weeks, the Lead will be completely converted into compact masses of White Lead, whilst the Acetic acid is barely changed and may be used again.

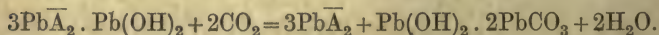
The chemical changes which occur are somewhat as follows: The heat of the fermenting tan volatilizes some of the Acetic acid, and this vapour attacks

the Lead, and, with the aid of Oxygen from the air, forms a basic Lead Acetate.

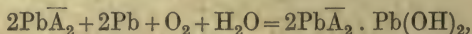
Writing $\overline{H\bar{A}}$ for Acetic acid (a convenient abbreviation for $H \cdot C_2H_3O_2$), the reaction may be represented thus:



This basic Acetate is then acted upon by the Carbon Dioxide gas evolved from the fermenting tan, forming White Lead and Lead Acetate:



The Lead Acetate and Oxygen act upon some more Lead, forming the basic Lead Acetate once more:



and so the process is continuous till all the Lead is changed to White Lead and only a very small quantity of Acetic acid is used up.

A more modern way of making White Lead consists in hanging "straps" of Lead in a brickwork chamber and subjecting them to a carefully regulated mixture of Water vapour, Carbon Dioxide and Acetic acid vapour. The chemical changes are similar to those which take place in the Dutch process, but the action goes on more quickly, and the resultant White Lead is claimed to be purer.

White Lead is very poisonous, and, also, will blacken in an atmosphere which contains even traces of Sulphuretted Hydrogen, but, so far, no substitute for it has been found for use in paints, which possesses anything like the same "body" or covering power.

Lead Acetate $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, often called "Sugar of Lead" because of its sweet taste, is a soluble Lead salt obtained by dissolving Litharge in Acetic acid. It is used considerably in the laboratory, both as a reagent and for various preparations. Like all Lead salts it is poisonous.

Detection of Lead. The presence of Lead in small quantities, as, for instance, in water contaminated with Lead, is best detected by bubbling Sulphuretted Hydrogen gas through the water, when a brownish colouration, produced by the precipitation of Lead Sulphide, is formed.

Lead salts give a white precipitate of PbCl_2 with Hydrochloric acid. This precipitate disappears on heating the liquid, but reappears, in crystalline form, as the liquid cools.

Yellow precipitates of PbI_2 and PbCrO_4 are formed by salts of Lead with Potassium Iodide and Chromate respectively. The former precipitate is soluble in hot water, but reprecipitates in golden "spangles" on cooling.

When heated on Charcoal, Lead salts give a metallic bead of Lead which is malleable and marks paper.

PROBLEMS.

69. Two Oxides of Tin contain 11.94 and 21.33 per cent. of Oxygen respectively. Shew that these numbers are in accordance with the Law of Multiple Proportions.

70. 1 gram of Pewter, containing Tin and Lead only, was acted upon by Nitric acid and the product converted into a mixture of Stannic Oxide and Litharge by strong heat. The weight of this mixture of Oxides was found to be 1.15 grams. Calculate the percentage composition of the Pewter.

71. In an experiment of Stas, 103 grams of pure Lead were converted into 164.775 grams of pure Lead Nitrate. If the Atomic Weights of Oxygen and Nitrogen are 16 and 14.04 respectively, calculate the Equivalent Weight of Lead, and, assuming its Specific Heat to be .03, determine its Atomic Weight.

PRACTICAL EXERCISES.

To obtain a specimen of Silica from Glass. Make an intimate mixture of powdered Glass with twice its weight of fusion mixture (Potassium and Sodium Carbonates). Place the mixture in a porcelain crucible (a Platinum crucible is better if available), and heat the crucible strongly with a blowpipe (or in a muffle furnace) for half an hour.

When cool, extract the Sodium (or Potassium) Silicate formed with hot water and filter away from any sediment. Add strong Hydrochloric acid till all effervescence of Carbon Dioxide gas ceases. Boil the clear liquid, and the Silicic acid,

liberated by the Hydrochloric acid, breaks up and gelatinous Silica is deposited.

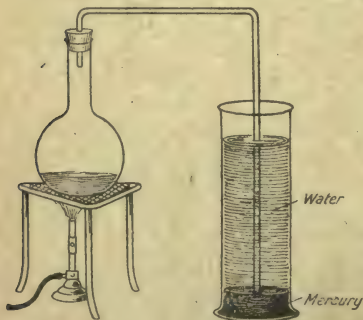
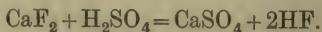


FIG. 135.—Preparation of Silicon Tetrafluoride.

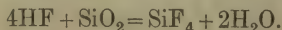
To prepare Silicon Tetrafluoride and obtain from it Gelatinous Silica. Make a mixture of Calcium Fluoride and white Sand. Put it in a flask and add sufficient strong Sulphuric acid to cover the mixture. Fit the flask with a cork and single delivery tube

running to the bottom of a gas jar. Put Mercury into the gas jar till it just covers the end of the tube, and fill the rest of the jar with water (Fig. 135). Warm the flask gently, and Silicon Tetrafluoride is evolved in the following manner:

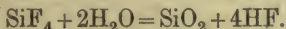
Hydrofluoric acid is first formed from the Calcium Fluoride and Sulphuric acid:



The Hydrofluoric acid attacks the sand, forming Silicon Tetrafluoride:



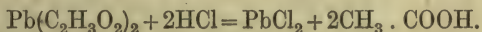
When the Silicon Tetrafluoride gas comes into contact with the water in the gas jar, the reverse operation occurs, and gelatinous Silica is deposited :



To make a Lead "Tree." Cut a piece of Zinc foil in the form of the letter T and suspend it in a gas jar containing a strong solution of Lead Acetate. Lead begins to be deposited at once, and after 4 or 5 hours, the crystals of Lead form the curious growth known as a "tree."

To test for Lead in Tap-water. If the laboratory water-pipes are made of Lead, the presence of dissolved Lead can be detected by drawing off into a boiling tube some of the water which has been standing overnight in the pipes and passing Sulphuretted Hydrogen gas through the liquid. A brown colouration caused by the precipitation of Lead Sulphide is usually formed.

To prepare crystals of Lead Chloride. Take a little Lead Acetate solution in a boiling tube ; add to it some dilute Hydrochloric acid. A white precipitate of Lead Chloride is formed :



↓

Boil the turbid liquid, when part of the precipitate will dissolve ; allow the rest of the precipitate to settle down, and pour off the clear liquid into another boiling tube. As the liquid cools, crystals of Lead Chloride, which are nearly insoluble in cold water, will be precipitated.

To prepare Lead Peroxide from Red Lead. Take about 10 grams of Red Lead in a boiling tube ; fill the tube half full with dilute Nitric acid and warm gently. The puce-coloured residue is Lead Peroxide, which may be separated from the liquid by filtration and dried in a cone over a sand bath.

CHAPTER XXVII.

THE ALKALI METALS.

FIVE metals—Lithium, Sodium, Potassium, Rubidium, and Caesium—which have well-marked similarities, both in the properties of the metals themselves and in their compounds, are included in a group which is usually known as that of the Alkali metals.

The name *alkali*, derived from the Arabic, and meaning the salt, was given to the salt obtained by treating the ashes of plants with water. This is now called Potash or Potassium Carbonate, and the use of the name was afterwards extended to other substances possessing similar “alkaline” properties. To distinguish between them various prefixes were used, *e.g.* “volatile alkali” for Ammonium Carbonate, “mineral alkali” for Sodium Carbonate, “vegetable alkali” for Potassium Carbonate, and “Caustic alkali” for the Hydrates of Potassium and Sodium, which were then indistinguishable.

The five metals of the Alkali Group are all soft silvery-white metals, easily cut and moulded, and they rapidly tarnish in air.

Their properties, both physical and chemical, exhibit a steady gradation from Lithium to Caesium, and, contrary to the usual custom in such groups, their activities increase with their Atomic Weights.

Thus, Lithium is attacked slowly by air, Sodium tarnishes in a few seconds, Potassium almost instantaneously, whilst Rubidium and Caesium take fire in air spontaneously.

Similarly in their action on water; with Caesium, Rubidium and Potassium, the heat developed is sufficient, even in cold

water, to ignite the Hydrogen evolved; with Sodium the Hydrogen is ignited if the water is hot, but, even in boiling water, Lithium does not ignite the Hydrogen.

All five metals are of low density; Lithium, Sodium and Potassium float on water, and the other two metals are slightly heavier than water.

Their melting points and boiling points decrease gradually, from 186°C . and 1400°C . in the case of Lithium to 26.5°C . and 670°C . in the case of Caesium.

The Hydroxides and Carbonates of all the five metals exhibit alkaline properties. Most of the salts of these metals with similar acids are isomorphous with one another, and practically all the salts of all the metals in this group are readily soluble in water, though Lithium Carbonate and Phosphate are less soluble than the others.

Only two members of the Group—Sodium and Potassium—are of sufficient importance for their properties and compounds to be discussed here.

SODIUM.

Symbol, Na (Natrium). Atomic Weight, 23.0.

Molecular Weight, 23.0.

Occurrence. Sodium is found very abundantly in nature as its Chloride, both dissolved in sea-water and various spring waters and also in enormous deposits of *Rock Salt*, which have probably been formed by the drying up of ancient seas and lakes. These deposits occur in Cheshire and Lancashire in England, and in many places all over the world. Large deposits of Sodium Nitrate, usually called *Chili Saltpetre*, are found in Chili and Peru, and Sodium is also found, as Sodium Silicate, in many minerals of volcanic origin.

Preparation. Both Sodium and Potassium metals were first prepared by Sir Humphrey Davy in 1807, by the action of a strong electric current on Caustic Soda or Caustic Potash. The operation is conducted in a Platinum crucible (Fig. 136), which is made the positive pole of the electrolytic operation and is suspended on a non-conducting porcelain triangle. The

negative pole, around which the metal collects, is a Platinum wire dipping into the Caustic Soda or Potash. The heat caused by the passage of the current is usually sufficient to melt the solid; if not, it may be heated by a small bunsen flame.

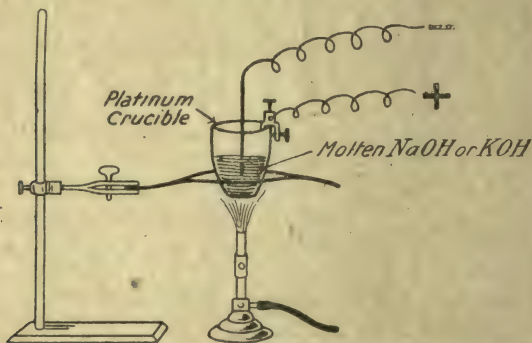
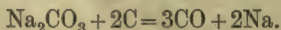


FIG. 136.—Davy's preparation of Metallic Sodium.

Metallic Sodium was, for a long time, obtained commercially by strongly heating a mixture of Sodium Carbonate and Charcoal in an Iron retort; the result was the production of Carbon Monoxide and Sodium vapour, which latter was condensed in an air-cooled Iron vessel:



Nowadays, Sodium is almost entirely obtained by electrolytic methods similar to Sir Humphrey Davy's. Two processes are in use:

(1) *Castner's Process*. In this, fused Caustic Soda is electrolysed in an Iron pot (Fig. 137). The cathode *C* is made of Carbon and is surrounded by the circular anode *A*, *A*, also made of Carbon. The Caustic Soda is kept in a molten condition, partly by the heat generated by the flow of the current, and partly by two small gas flames *F*, *F*. The Sodium from the cathode rises into the receptacle *H*, which is opened from time to time, and the Sodium is ladled out. Hydrogen is also evolved from the cathode, and this escapes through the

cover of *H*, whilst the Oxygen given off at the anode escapes through *O*.

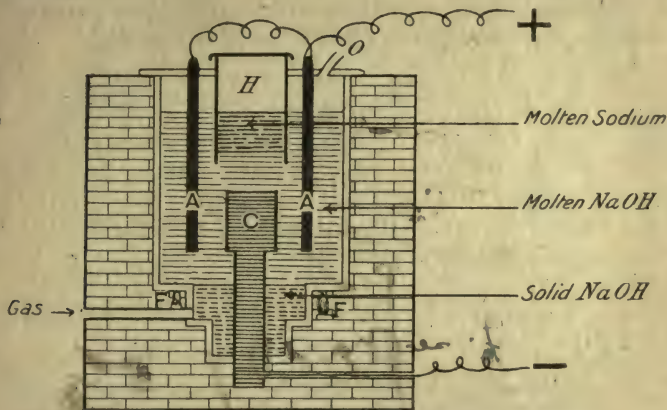


FIG. 137.—Castner's process for obtaining Metallic Sodium.

(2) *Borcher's Process*. In this process fused Salt is electrolysed. It is more economical than Castner's process, because no energy is lost by the evolution of Hydrogen at the cathode; also the bye product, Chlorine, evolved at the cathode, can be used for making Bleaching powder.

The operation is conducted in a U-tube (Fig. 138), one half of which is made of Iron

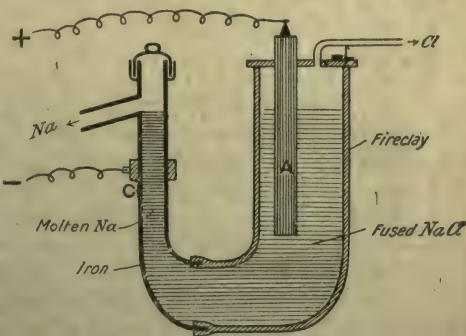


FIG. 138.—Electrolysis of Fused Salt. (Diagrammatic.)

and acts as the cathode, and the other wider half is made of fireclay and contains a Carbon anode *A*. The process is

continuous, fresh Salt being introduced, from time to time, through a lid *L* in the fireclay portion of the tube.

Properties. Sodium is a bright lustrous metal, so soft that, at ordinary temperatures, it can be readily moulded between the fingers. It becomes brittle at -20°C .

It is rapidly attacked on exposure to air, forming a film of Oxide, which first absorbs water, forming the Hydroxide, and then Carbon Dioxide, forming a white coating of Sodium Carbonate. To prevent this, metallic Sodium is usually preserved under Petroleum or Naphtha.

Sodium melts at 97°C ., and boils at 877°C ., forming a violet-coloured vapour. The density of this vapour is about 12 ($H=1$); this corresponds to a molecular weight of 24, and as 23 is usually accepted as the atomic weight of Sodium, its vapour must be monatomic.

Sodium burns when heated in air, forming Sodium Peroxide, Na_2O_2 , but, if the air is perfectly dry, this action does not take place.

The action of Sodium on water has already been noted; the violence of this action is much reduced by first amalgamating the Sodium with Mercury, a process very simply accomplished by rubbing, with a pestle, small pieces of Sodium into contact with a globule of Mercury contained in a mortar.

Acids, both strong and dilute, act upon Sodium with great violence, evolving Hydrogen and forming the Sodium salt of the acid.

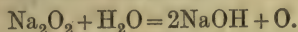
COMPOUNDS OF SODIUM.

Oxides. Sodium forms two Oxides, the Monoxide, Na_2O , and the Peroxide, Na_2O_2 .

Sodium Monoxide is formed, along with the Peroxide, when the metal is heated in a limited quantity of air. It combines at once with the water in the atmosphere, forming the Hydroxide.

Sodium Peroxide is formed when Sodium is heated in a stream of air or Oxygen. It is white, when pure, but the commercial product is usually yellow.

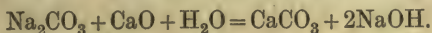
In the presence of water, the Peroxide is decomposed, yielding Caustic Soda and Oxygen gas :



On this account, it is a powerful Oxidizing agent, and is useful for this purpose in the laboratory and also for bleaching straw and other delicate fabrics.

Sodium Hydroxide, Caustic Soda, NaOH. This most important compound of Sodium is made in two ways :

(1) By boiling a solution of Sodium Carbonate with Lime :



↓

Chalk is precipitated, and the solution of Caustic Soda is decanted and concentrated by boiling in Cast-Iron pans.

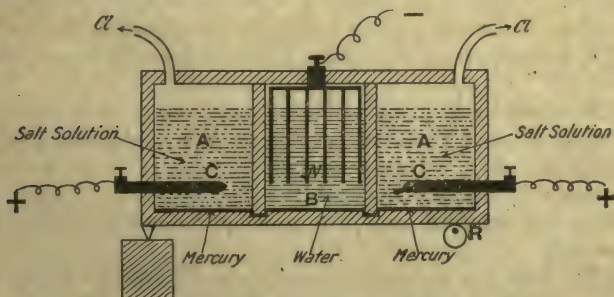


FIG. 139.—Manufacture of Caustic Soda.

(2) By the electrolysis of a solution of Salt. The process is seen in the diagram (Fig. 139). There is a rectangular vessel, divided into three parts; the two outer portions, *A, A*, contain a strong solution of Salt and the inner partition, *B*, contains water. The divisions between the partitions are not complete, but the liquids are prevented from mixing by a thin layer of Mercury covering the floor.

The chemistry of the process is as follows: The Sodiums proceeding from the Carbon anodes, *C, C*, go first to the Mercury on the floor and form an amalgam with it. By means of an eccentric rocker, *R*, this amalgam is caused to flow, to

and fro, along the bottom, and eventually it comes into the central portion, - *B*, containing an ^{CATH}ode, *N*, made of metal plates. Here the amalgam is attacked by the water, Hydrogen is evolved, and Caustic Soda goes into solution, which is taken out, from time to time, when sufficiently concentrated, and fresh water substituted. Chlorine is evolved at the anodes, and may be used for a variety of purposes.

Sodium Hydroxide is a white crystalline substance, usually sold in sticks. It rapidly absorbs water and Carbon Dioxide from the air, and is used as an absorbent of this latter gas. It is very soluble in water, a considerable amount of heat being evolved during the process of solution.

Large quantities of Caustic Soda are used in manufacturing processes such as bleaching, dyeing, oil refining and soap-making.

Sodium Chloride NaCl. Common Salt is one of the most abundant chemical compounds found on the earth. As Rock Salt it occurs in beds, which are sometimes of vast proportions. The one in Galicia is said to be 500 miles long, 20 miles broad and 1200 feet thick; it has been worked continuously for 500 years. Beds are found in England at Nantwich, Northwich and Middlewich in Cheshire, and Droitwich in Worcestershire. The ending "wich" denoted, in Saxon times, a place where Salt was dug out. Rock Salt beds are also found in numerous localities in the United States, in Spain and in many other places.

It is also found dissolved in sea-water, to the extent of about 27 parts per 1000, and, in countries where natural beds of Salt do not occur, is obtained from this source. Where coal is cheap, the sea-water may be evaporated by heating; in warm countries, such as the shores of the Mediterranean, the sea-water is caused to flow into shallow basins, called Salterns, where the sun and wind cause the water to evaporate; in cold countries, such as the shores of the White Sea, the sea-water is first concentrated by freezing; as the ice which is formed contains very little salt, this ice is removed and the remaining solution evaporated by heating.

The Rock Salt is either mined direct, as in Galicia, or water

is introduced down to the Salt bed by means of a boring, and, after a time, pumped up and the "brine" evaporated for the Salt. This taking away of Salt from underground causes the subsidences which are so common in towns in Cheshire, where Salt is obtained by this method.

Salt obtained by any of these methods is never quite pure, though Cheshire Salt contains over 98 per cent. of Sodium Chloride. If the pure substance is required, it may be obtained by adding Hydrochloric acid to a strong solution of the impure Salt, when Sodium Chloride crystallizes out and the impurities are left in the solution.

Sodium Chloride crystallizes in colourless cubic crystals, which contain no water of crystallization, but, if crystallized at -10°C. , the crystals formed contain two molecules of water, which, however, they lose when exposed to the air.

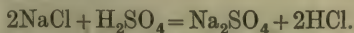
Its solubility may be seen by referring to the diagram on p. 86; its very small increase with rise of temperature is a curious feature.

Salt is necessary for the food of man and other animals. It furnishes, amongst other things, the Hydrochloric acid present in the gastric juices so important in digestion. It is used for preserving meat and fish, for the manufacture of Washing Soda and Soap, and as "Salt glaze" for the glazing of common pottery.

Sodium Carbonate, Washing Soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The manufacture of this substance forms one of the most important industries—the alkali manufacture. It is performed by three methods, all of which are still used: (1) The Leblanc process, (2) The Solvay or Ammonia-Soda process, and (3) The Electrolytic method.

The Leblanc Process. This process contains three stages:

(1) Common Salt is converted into Sodium Sulphate by strongly heating in a furnace with the proper quantity of concentrated Sulphuric acid:



The solid product is called "*Salt cake*," and the Hydrochloric acid fumes are dissolved in water and form an important by-product.

(2) The Salt cake is mixed with Limestone and Coal and the mixture heated to a high temperature in a revolving cylinder, through which the flames from a reverberatory furnace pass (Fig. 140).

The Sodium Sulphate is probably first reduced to Sodium Sulphide, Na_2S , by the coal, and this substance reacts with

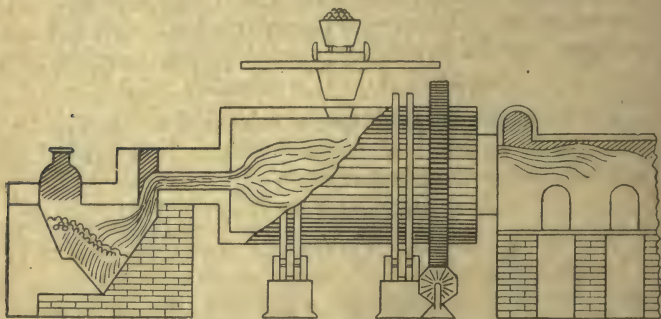
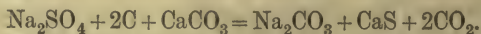


FIG. 140.—The "Black Ash" process.

the Limestone, forming Calcium Sulphide and Sodium Carbonate. The two reactions are represented together in the equation :

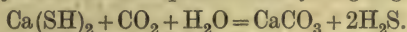


The liquid mass is drawn out of the cylinders and forms, on solidification, a dark grey substance known as *black ash*.

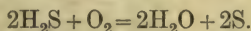
(3) The black ash is ground to powder, and then lixiviated with as small a quantity of water as practicable in a series of tanks. Fresh water acts upon ash, from which nearly all the Carbonate has been extracted, and water, which is nearly saturated, acts upon ash fresh from the furnace. By this means all the Sodium Carbonate is dissolved, and when the solution is allowed to settle, the "tank waste" contains the Calcium Sulphide, excess of Carbon and other impurities. When the clear liquid is evaporated and calcined, *i.e.* heated very strongly, the product is called crude Soda ash, and

contains mainly Na_2CO_3 . This substance is dissolved in hot water and allowed to crystallize, and the product is Soda crystals or Washing Soda $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

An important item in the Leblanc process is the Sulphuric acid, which is apparently lost, but, by *Chance's Process*, Sulphur is recovered from the tank waste and can be used for the manufacture of more Sulphuric acid. This process consists in forcing Carbon Dioxide gas through the tank waste suspended in water. By this means Sulphuretted Hydrogen gas is evolved:



The Sulphuretted Hydrogen is mixed with sufficient air to burn the Hydrogen, but not the Sulphur; Iron Oxide is used as a Catalyst in this latter reaction:

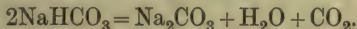


The Solvay or Ammonia-Soda Process. In this process a concentrated solution of Salt is saturated with Ammonia gas; the liquid is cooled and allowed to pass slowly down a tower, where it meets an upward stream of Carbon Dioxide gas, whose progress up the tower is impeded at intervals by perforated discs to ensure its complete absorption. The following reaction takes place:

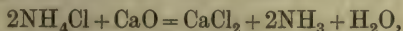


The Sodium Bicarbonate and Sal-Ammoniac formed have different degrees of solubility, so much so that, if the solution is properly concentrated, the Bicarbonate separates out as minute crystals and can be removed by filtration.

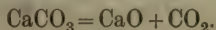
When Sodium Carbonate is needed, the Bicarbonate is calcined:



The process is most economical, as the Sal-Ammoniac can be boiled with Lime, and so the Ammonia is recovered:



and the Carbon Dioxide required can be obtained by heating Limestone, the Lime, which is made at the same time, serving for the recovery of the Ammonia:



Thus, for this process, only Limestone and Salt—both very cheap substances—and a small supply of Sal-Ammoniac are necessary, and this latter substance does not, theoretically, require renewal, whilst the only bye-product is Calcium Chloride, and an endeavour has lately been made to use this substance for laying the dust on roads.

The Electrolytic Process. In this method a solution of Salt is subjected to electrolysis in a special form of apparatus, a diagrammatic bird's-eye view of which is seen in Fig. 141. This represents an oblong box, divided lengthways, by two asbestos partitions, into three portions, a wide central part and two narrow divisions near the sides. The central part contains the salt solution, and in it several Carbon anodes

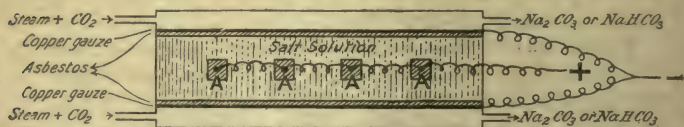
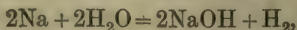
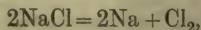
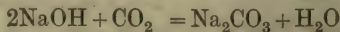


FIG. 141.—Electrolytic process for making Sodium Carbonate. (Diagrammatic.)

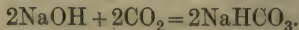
(A, A) are suspended. The asbestos is sufficiently pervious to allow the Salt solution to soak slowly through, and is coated on the outside with large mesh Copper gauze, which serves as the cathode. During electrolysis metallic Sodium is deposited on the gauze, but is immediately swept away by a current of Steam and Carbon Dioxide, which is passed through the outer divisions. The Steam first forms Caustic Soda with the Sodium, and this substance unites with the Carbon Dioxide to form either Sodium Carbonate or Sodium Bicarbonate, according to the amount of Carbon Dioxide present, which amount is regulated by the salt which is required. The equations representing the various actions are :



and either



or



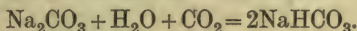
The Sodium Carbonate manufactured by this process at Middlewich is remarkably pure, containing about 98 per cent. of the pure compound.

The Chlorine evolved at the anode can be made use of for Bleaching Powder, etc.

Sodium Carbonate forms transparent crystals, containing ten molecules of water of crystallization. On exposure to air, it effloresces, losing nine of these molecules and leaving a white powder $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

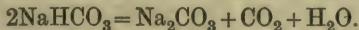
It is used in enormous quantities for various purposes in the arts, and one of its main uses is to cleanse the fat and grease from dirty plates which have been used for meals. This it brings about by its power to "*emulsify*" the fat, *i.e.* cause it to split up into thousands of very tiny separate globules, which are readily washed away.

Sodium Bicarbonate, Sodium Hydrogen Carbonate, NaHCO_3 . This substance may be obtained by passing Carbon Dioxide through a solution of the normal Carbonate :



Owing to the fact that it is much less soluble in water than the normal Carbonate, it is deposited first from a solution containing both.

It is made in large quantities by the Solvay process described above, and is used as a medicine, for making Carbonic Acid gas and for baking powder. Its use as a baking powder depends upon the fact that a very gentle heat is sufficient to decompose the Bicarbonate, and, as it evolves Carbon Dioxide when it decomposes, the bubbles of gas cause the cake to "rise":



Sodium Sulphate, Glauber's Salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is found native in small quantities, and is readily made by acting upon the Chloride or Carbonate of Sodium with Sulphuric acid. It crystallizes in colourless prisms containing ten molecules of water, and the solubility of these crystals has already been discussed (p. 85). It is used as a medicine.

Sodium Nitrate NaNO_3 . This compound is found in beds in Peru, Chili and Bolivia on the western coast of South America.

It is mixed with a certain amount of earthy matter and other impurities, but the richest part of the bed, which is called "*caliche*," may contain up to 50 per cent. of Sodium Nitrate. The origin of this bed of Chili Saltpetre, as it is usually called, is unknown; its preservation is due to the fact that the district is practically rainless.

Sodium Nitrate occurs in rhombohedral crystals, which are a little deliquescent and become damp in air. This prevents its use for gunpowder and other explosives. It is, however, used most extensively for manure, and the countries in which it is found derive a large part of their national income from the sale of it.

Phosphates of Soda. Of the three Sodium Orthophosphates (p. 292), the only one which is prepared in any quantity is di-Sodium mono Hydrogen Phosphate Na_2HPO_4 , which is formed by the neutralization of Caustic Soda solution with Phosphoric acid. It forms colourless crystals of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, which effloresce in air. It is used in some of the liquid preparations for the extinction of fires and for rendering lace curtains and similar fabrics non-inflammable.

Detection of Sodium. Sodium salts give an intense yellow colouration to the bunsen flame, but, as small impurities of Sodium are present in many salts, this test is not convincing. Owing to the fact that all Sodium salts are soluble in water, no precipitates can be formed with any reagent whatever, so the detection of this metal is never certain. It is usual to infer its presence when

- (1) No other metal has been discovered.
- (2) The substance is crystalline and soluble in water.
- (3) It gives an intense yellow colour to the flame.

POTASSIUM.

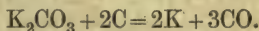
Symbol, K (Kalium). Atomic Weight, 39.1. Molecular Weight, 39.1.

Occurrence. When the ashes formed by burning wood are first digested with water and the solution is evaporated to dryness in an Iron pot, the residue is Potash, and consists mainly of Potassium Carbonate.

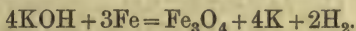
Potassium is of common occurrence in the tissues of plants, either as Oxalate or Carbonate; it is also found in the substance known as *Suint*, which is extracted by water from the wool of sheep. Potassium Nitrate is found along with Sodium Nitrate in the Chili beds, but the largest known deposit of Potassium compounds is found at Stassfurt in Germany. Here the chief constituents of the beds are *Sylvine*, Potassium Chloride, KCl , *Carnallite*, a double Chloride of Potassium and Magnesium, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and *Kainite*, a mixed Sulphate and Chloride, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. This latter substance is used as a fertilizer.

Preparation. Potassium metal is not prepared in the same quantities as Sodium, but the methods used are very similar.

(1) It is formed when Potassium Carbonate is heated strongly with Charcoal:



(2) It is also obtained by allowing melted Potassium Hydroxide to pass over white hot Iron turnings:



(3) The modern method is merely an adaptation of Sir Humphrey Davy's method, the electrolysis of fused Caustic Potash. It is performed in exactly the same apparatus as for Sodium.

Properties. The properties of metallic Potassium are very similar to those of Sodium, except that it is a little more active towards reagents. For example, it tarnishes instantaneously in air, it ignites the Hydrogen which it displaces from water, and it takes fire spontaneously in Chlorine or Bromine vapour.

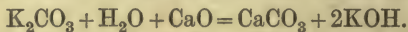
It melts at 62°C ., and boils at 700°C ., forming an emerald-green vapour. This vapour at 1000°C . has a density of about 21. This indicates a molecular weight of 42, and the vapour molecule is therefore monatomic, as analysis indicates an Atomic Weight of 39.1 for Potassium.

Heated Potassium will burn in Carbon Dioxide, forming Potassium Carbonate and Carbon. When heated in Hydrogen gas, Potassium forms a brittle Hydride, K_4H_2 , which takes fire spontaneously in air.

COMPOUNDS OF POTASSIUM.

Oxides. When Potassium is heated in a limited amount of air, the Monoxide, K_2O is formed. If the metal is melted in an atmosphere of Nitrogen gas and then Oxygen is slowly admitted, it forms the Tetroxide, K_2O_4 , a chrome-yellow powder.

Potassium Hydroxide, Caustic Potash, KOH. This compound is made in a precisely similar manner to Caustic Soda, that is, either by the electrolysis of a solution of Potassium Chloride or by boiling Potassium Carbonate solution with Lime :

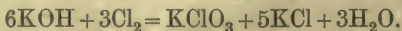


↓

Caustic Potash is a white solid resembling Caustic Soda in every respect, both physically and chemically. Either of these two substances may be used as a substitute for the other in any chemical action where the difference of metal is immaterial.

Potassium Chloride KCl is similar in all respects to Sodium Chloride, with which salt it is isomorphous.

Potassium Chlorate $KClO_3$. This compound is formed, as has already been seen (p. 197), when Chlorine gas is introduced into a hot concentrated solution of Caustic Potash :



On cooling, the less soluble Chlorate crystallizes out whilst the Chloride remains in solution.

As will be seen from the equation, the process is a wasteful one, as only one-sixth of the Potassium in the Caustic Potash used is converted into Chlorate.

Nowadays, as in so many chemical preparations, Potassium Chlorate is manufactured by an electrolytic process. A hot solution of the Chloride is subjected to the action of an electric current in a cell constructed so that the substances formed at both anode and cathode are brought into contact with one another by stirring. In this way the Chlorine evolved at the anode reacts with the Caustic Potash formed at the cathode, and the ultimate product is Potassium Chlorate. This, being but sparingly soluble in water, crystallizes out and gives trouble,

so that it is now usual to form Sodium Chlorate by a similar process and mix it with Potassium Chloride. Since the solubility of Sodium Chlorate at 20° is 99, whilst that of Potassium Chlorate at the same temperature is but 7, if a solution containing these compounds is slowly evaporated, the first crystals to be deposited will be those least soluble, namely, those of Potassium Chlorate.

Potassium Chlorate forms white tabular crystals, which have no water of crystallization. Owing to the ease with which it parts with its Oxygen, it is used in the manufacture of matches, fireworks and explosives generally. It is also used as a medicine.

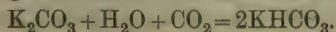
Potassium Carbonate K_2CO_3 . This substance is still obtained in certain parts of Canada and the United States by lixiviating wood ashes and calcining the residue formed when the solution is evaporated. By allowing some of the less soluble substances to crystallize out and then evaporating the "mother liquor," a purer product, called by Americans "*pearl ash*," is obtained.

Potassium Carbonate is also obtained from "*suint*" (p. 289). The water in which sheep's wool has been washed is evaporated and the solid residue calcined. The carbonaceous residue is extracted with hot water, and Potassium Carbonate is obtained from this solution.

Since the discovery of the Stassfurt beds and consequent cheapness of Potassium Chloride, Potassium Carbonate is obtained from the Chloride by a process strictly similar to the Leblanc process for making Washing Soda. The Solvay process cannot be used, as the difference in the solubilities of Potassium Bicarbonate and Ammonium Chloride is not sufficient to ensure separation.

Potassium Carbonate is used in the manufacture of certain kinds of Glass, but is not by any means so important a substance as Sodium Carbonate.

Potassium Hydrogen Carbonate, Bicarbonate of Potash, $KHCO_3$. This compound is made in a precisely similar manner to the corresponding Sodium Bicarbonate, by passing Carbon Dioxide gas through a solution of the Carbonate :

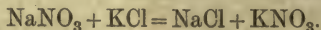


As it is less soluble than the Carbonate, it can be separated by fractional crystallization.

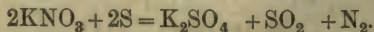
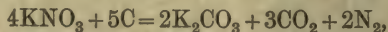
Potassium Nitrate, Nitre, Saltpetre, KNO_3 . Deposits of Potassium Nitrate are found in beds, like Sodium Nitrate, but only to a much smaller extent.

When beds containing Nitrogenous matter, such as manure, urine or dung, are exposed to the air, if certain organisms are present (and only in their presence), the Ammonia in the refuse is oxidized, first to Nitrous acid and then to Nitric acid, by two different ferments. These acids, in the presence of Potassium Carbonate from the vegetable refuse matter, form Potassium Nitrate, which appears as a scum or efflorescence on the surface of the refuse heap. This is taken off, the Nitre extracted by water and purified by recrystallization. The process may occur naturally or be made to occur artificially in the so-called Nitre plantations, which are fairly common in the hot, dry Eastern countries—India, Persia, Arabia, etc.

Nowadays, Potassium Nitrate is obtained from Chili Saltpetre by mixing a solution of this salt with Potassium Chloride obtained from the Stassfurt beds. If the resulting solution is evaporated by passing steam through it, the Sodium Chloride, being least soluble at this temperature, is first precipitated and removed, and on cooling, crystals of Potassium Nitrate are obtained :



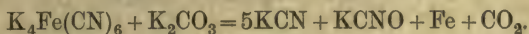
Potassium Nitrate forms rhombic prisms which have no water of crystallization. It melts at 339°C ., and at higher temperatures evolves Oxygen, leaving behind Potassium Nitrite. Small pieces of Charcoal or Sulphur take fire when thrown upon molten Saltpetre, and burn vigorously. The reactions which occur are probably represented as follows :



Saltpetre is used largely for making gunpowder and fireworks generally ; in small quantities it is used as a medicine.

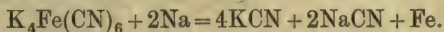
Potassium Cyanide KCN . This compound was formerly

made by heating Potassium Ferrocyanide (yellow Prussiate of Potash) with Potassium Carbonate to a red heat :



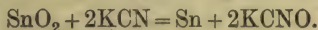
The soluble Cyanide and Cyanate are dissolved out with water, the solution evaporated and the Cyanide cast into sticks.

Nowadays, a mixture of Sodium and Potassium Cyanides is made by fusing the Ferrocyanide with metallic Sodium :



Potassium Cyanide is a white crystalline solid, which dissolves readily in water. Its solution has an alkaline reaction, owing to the "weak" Hydrocyanic acid which is formed by hydrolysis. For the same reason, both the solid substance and the solution smell of Prussic acid, and are equally poisonous.

Potassium Cyanide is used largely for electro-plating and gilding, for the extraction of Gold from Quartz and in photography. When in a molten state, it absorbs Oxygen readily, forming Potassium Cyanate KCNO, and, on this account, is used for reducing metallic Oxides on Charcoal, *e.g.* :



Detection of Potassium. Practically all the salts of Potassium are very soluble in water, but certain double salts of Potassium and other metals are less soluble, and consequently will yield precipitates. Thus, Platinum Chloride gives a yellow crystalline precipitate of Potassium Platinochloride K_2PtCl_6 ; Sodium Cobalti-nitrite in the presence of Acetic acid gives a yellow crystalline precipitate of Potassium Sodium Cobalti-nitrite, $\text{K}_2\text{NaCo}(\text{NO}_2)_6$.

Potassium compounds give a lilac colour to the bunsen flame.

AMMONIUM.

As has been seen already (p. 250), Ammonia gas forms a series of salts with acids which are called Ammonium salts; and are supposed to be salts of a mono-valent radicle NH_4 .

These salts are found to be isomorphous with the corresponding Potassium salts, so they are conveniently studied here.

When a strong solution of an Ammonium salt is electrolysed in such a way that the cathode dips under Mercury

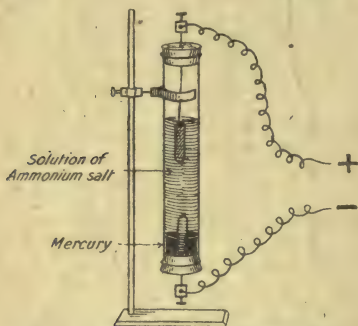
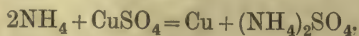


FIG. 142.—Formation of Ammonium Amalgam.

(Fig. 142), the Mercury swells up, forming a frothy mass, which is called Ammonium Amalgam. If the temperature is kept below 0°C ., the froth is not so pronounced, the Amalgam appearing as a slimy mass.

It is supposed that this substance is a solution of Ammonium in Mercury, which breaks up into the froth at temperatures above 0°C ., as the froth itself obeys the usual laws of gases—Boyle's Law, etc.—and is found to consist of a mixture of Ammonia gas and Hydrogen, entangled in the Mercury. One potent reason for considering the mass—below 0°C .—to be a true Ammonium Amalgam is that it will displace metals, like Copper and Zinc, from their Sulphates, thus:



Neither Ammonia gas nor Hydrogen will bring about such a displacement.

AMMONIUM SALTS.

The chief source of all the salts of Ammonium is the Ammoniacal liquor from gas-works. This liquor is boiled with Lime to drive off Ammonia gas, which is led into Sulphuric or Hydrochloric acid, forming the Sulphate or Chloride of Ammonium.

Ammonium Chloride, Sal-Ammoniac, NH_4Cl . Crude Sal-Ammoniac is prepared by the process just indicated. It is purified by *Sublimation*; the impure substance is heated in large iron or earthenware pots (Fig. 143) having a dome-

shaped cover, on which the purified substance sublimes, whilst the impurities remain behind.



FIG. 143.—Sublimation of Sal-Ammoniac.

Ammonium Chloride forms beautiful fern-like crystals, which dissolve readily in water, with a sensible lowering of temperature. The solution dissociates to some extent when boiled.

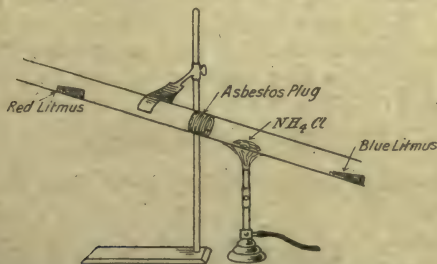


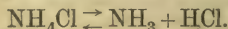
FIG. 144.—Dissociation of Ammonium Chloride.

Some of the Ammonia escapes with the steam, and the resulting liquid is slightly acid.

When vaporized, the vapour density of Ammonium chloride is found to be half what it should be for the formula NH_4Cl ; this is because the molecule dissociates almost at once into two molecules, of Ammonia and Hydrochloric acid gas.

That this dissociation does take place can be readily shewn

by heating some of the solid substance in a slightly inclined tube (Fig. 144) which has an asbestos plug in the centre. Some red litmus paper placed in the upper half of the tube is turned blue by the lighter Ammonia gas, and some blue litmus paper in the lower half is turned red by the heavier Hydrochloric acid gas :



Ammonium Chloride is used for charging Leclanché cells, both wet and dry, and in many textile industries.

Ammonium Sulphate $(\text{NH}_4)_2\text{SO}_4$, prepared from gas-works liquor by absorbing the Ammonia in Sulphuric acid, is very much used as a chemical manure to supply the necessary Nitrogen for growing crops.

Ammonium Carbonate $(\text{NH}_4)_2\text{CO}_3$. The commercial compound is made by heating a mixture of Ammonium Sulphate and powdered Chalk in iron retorts and condensing the vapours as a white sublimate. This sublimate, even when re-sublimed, contains Ammonium Carbamate, $\text{NH}_4\text{CO}_2\text{NH}_2$, as well as the Carbonate; it is usually called *Sal-Volatile*, and is much used as a basis for smelling salts, owing to the fact that it is always giving off Ammonia gas.

Ammonium Nitrate NH_4NO_3 , prepared by leading Ammonia gas into Nitric acid, is used largely for producing low temperatures when it is dissolved in water. A temperature of -15°C . is easily obtained by this means. It is also used for the making of Nitrous Oxide gas.

Detection of Ammonium. All Ammonium salts yield Ammonia gas when boiled with Caustic Potash, which gas is easily detected by its smell and alkaline reaction.

With Platinum Chloride and a little dilute Hydrochloric acid, a yellow crystalline precipitate of Ammonium Platino-Chloride, $(\text{NH}_4)_2\text{PtCl}_6$, is obtained, very similar to the Potassium compound.

With Nessler's solution—a solution of Mercuric Iodide in Potassium Iodide and Caustic Potash—a brown precipitate or colouration is formed, even in very dilute solutions. This is a very delicate test, and will indicate the presence of 1 part of Ammonium in 100,000 of water.

PROBLEMS.

72. One gram of Soda Ash, treated with Hydrochloric acid, evolved 150 c.c. of Carbon Dioxide at 0° C. and 760 mm. Determine the percentage of Sodium Carbonate in the Soda Ash.

73. .9330 gram of a mixture of the Chloride and Iodide of Sodium was converted completely into Sodium Sulphate, which weighed .9066 gram. Find the weights of Sodium Chloride and Sodium Iodide in the mixture. (Camb. Univ. Schol. Exam.)

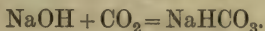
74. What volume of Carbon Dioxide gas is evolved at 30° C. and 740 mm. when 50 grams of Potassium Bicarbonate is strongly heated ?

PRACTICAL EXERCISES.

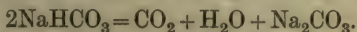
To shew the action of Sodium Carbonate as an "Emulsifier" of Oils. Take about 2 inches of water in a test tube and add to it 1 inch of Olive oil. Place the thumb over the top of the tube and shake vigorously. If the test tube is now set aside for a short time, the two liquids separate out into distinct layers.

Now place about a gram of powdered Sodium Carbonate in the tube and again shake vigorously. The result is a creamy "emulsion," and the liquids do not again separate out into two layers on standing.

To prepare the Bicarbonate and Carbonate of Sodium. Fill about two-thirds of a boiling tube with a *strong* solution of Caustic Soda. Bubble Carbon Dioxide gas through the liquid till no more is absorbed. The liquid becomes hot owing to the chemical union of the two substances, and, on cooling, will deposit Sodium Bicarbonate as a white powder :



Filter away from the Bicarbonate and boil the filtrate vigorously for 5 minutes. The Bicarbonate in the solution splits up into Carbon Dioxide, Water and Sodium Carbonate :



Crystals of Sodium Carbonate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ can be obtained from the resultant liquid by allowing it to cool.

To determine the Equivalent Weight of Sodium Bicarbonate. Dry a few grams of Sodium Bicarbonate in a desiccator, *not* by heating, and proceed to find its Equivalent Weight by precisely the same method as used for Potassium Carbonate (p. 53).

To shew that Saltpetre is a Supporter of Combustion. Melt a few grams of Saltpetre in a test tube and drop into the molten liquid small pieces of roll Sulphur and Charcoal which have been made red hot in the flame.

To shew the Dissociation of Ammonium Chloride Vapour. Perform the experiment described on page 395 (Fig. 144).

To prepare some Ammonium Amalgam. Take about 50 c.c. of a strong solution of Sal-Ammoniac in a beaker, add a small quantity of Sodium Amalgam (see p 192), the metallic froth formed is Ammonium Amalgam. Keep it for an hour or two in water and notice what happens.

CHAPTER XXVIII.

COPPER, SILVER AND GOLD.

ON referring to the table of the Periodic Series of the elements (p. 137), in the same group as the Alkali metals are found the three metals Copper, Silver and Gold. It is quite impossible to classify these metals with the Alkali metals, owing to the great dissimilarity in their properties. For instance, Silver and Gold are quite unacted upon by air, and Copper only to a limited extent; neither water nor steam has any action upon any of these three metals. They are all very heavy, whilst the Alkali metals are very light. Cold Hydrochloric or Sulphuric acids have no action on either Copper, Silver or Gold, etc., etc. In fact, their only point of resemblance to the Alkalies is that in some of their compounds they are mono-valent.

The similarity between the three metals themselves is by no means marked. They are all malleable and ductile metals, and shew a gradation in this property, the malleability of Silver being less than that of Gold, but greater than that of Copper. In tenacity, the reverse is the case, Copper being the most and Gold the least tenacious; also their densities increase in gradation: Copper 8.9, Silver 10.5 and Gold 19.2.

They have a series of similar compounds in which all three metals shew mono-valency, *e.g.* Cu_2O , Ag_2O , Au_2O ; Cu_2S , Ag_2S , Au_2S ; CuCl , AgCl , AuCl , but the more common compounds of Copper, such as CuO , CuSO_4 , show di-valency, and the best known compounds of Gold, *e.g.* Au_2O_3 , AuCl_3 , are tri-valent. Cuprous and Argentic Chlorides are insoluble in water, whilst Aurous Chloride is decomposed by water.

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It is clear that they are not a well-marked group of elements, but, for convenience' sake, they are usually studied together.

COPPER.

Symbol, Cu (Cuprum). Atomic Weight, 63.6.

History. Probably owing to the fact that Copper is found native to some extent, this metal has been known from pre-historic times, and was used by man in those times for weapons and for utensils. The "copper" age followed the "stone" age in historic sequence: The Romans obtained the metal from the Isle of Cyprus; hence the name *Cuprum* for this element.

Occurrence. Metallic Copper is found in enormous masses in Michigan on the shores of Lake Superior, and in smaller quantities in other places, such as Cornwall, Siberia and Australia.

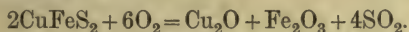
In combination Copper is found abundantly, usually as Oxide, Sulphide or Carbonate. A few of the better known ores are *Cuprite* or ruby ore, Cu_2O , *Copper Glance*, Cu_2S , *Copper Pyrites*, CuFeS_2 , *Malachite*, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ and *Azurite*, $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$.

It must be borne in mind by the student that the formulae of minerals, such as those given above, represent the very purest form of the mineral, and that pure minerals are a rarity. The Sulphides and Carbonates of Copper are usually highly complex mixtures, and the definite formulae given above are just a matter of convenience.

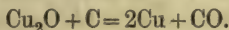
Preparation. The most abundant ores of Copper are those containing Sulphide of Copper, and these ores contain, as a rule, a large percentage of other metals such as Iron, Silver and Gold. The process of Copper extraction is therefore a very complicated one, and only an idea of the chemistry of the method of its extraction from Copper Pyrites will be considered.

(1) The Pyrites is first crushed, the earthy matter is washed away and the concentrated ore is roasted in a current of air in a reverberatory furnace (p. 362). This has the effect of

converting the Sulphides into Oxides, the Sulphur being driven off as Sulphur Dioxide :



This roasted ore is then mixed with some unroasted ore and Coke, and heated in a blast furnace. Various actions probably occur. The Cuprous Oxide is reduced to Copper by the Coke :



This Copper unites with some Sulphur from the unroasted ore forming Cuprous Sulphide, Cu_2S . Part of the Iron unites with the Silica which was probably present in the original ore

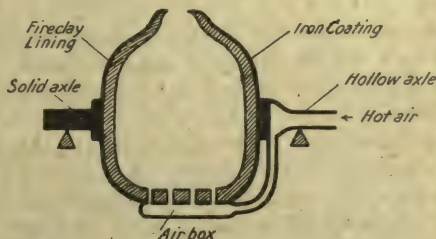


FIG. 145.—A converter.

(if not, some Sand is added) forming a fusible slag which may be removed.

The ultimate result is the production of a mixture of Cuprous and Ferrous Sulphides which is called *Matte*, which is drawn off from time to time. The molten *Matte* is run into a "converter" furnace (Fig. 145), lined with a mixture of white sand and clay, and arranged with openings in the base, by which hot air can be blown through the molten mass. The Sulphur and Iron are first oxidized, the Iron Oxide unites with the Sand to form a slag, and molten Copper remains at the bottom of the converter. This is then tilted and the Copper run out. The molten Copper dissolves Sulphur Dioxide gas, but, as the metal solidifies, the gas is expelled in the form of bubbles, giving the metal a blistered appearance ; hence the product is called *Blister Copper*.

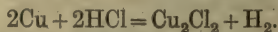
Blister Copper is purified by melting it in a furnace and then stirring the molten mass with a log of green wood. The process is called "poling," and the Hydrocarbon gases expelled from the wood by the heat reduce any Oxide of Copper present to the metal. The resultant substance is called Crude Copper.

Crude Copper is further refined by electrolysis. Plates of it are hung, as anodes, in a bath of Copper Sulphate solution, and the cathodes consist of thin sheets of pure Copper. When the current is passed, the Copper passes from the anode to the cathode, and the impurities in the Crude Copper fall from the anode, forming "anode mud." Considerable quantities of Silver and Gold are obtained from this mud. The Copper is deposited on the cathode plate, is very pure, and often contains as much as 99.8 per cent. of Copper. This state of purity is highly important when the metal is to be used for electrical purposes, as a very small percentage of impurity causes a comparatively large decrease in its electrical conductivity.

Properties. Copper has a characteristic colour and lustre, which can best be described by the term "copper-coloured." It occurs native in octohedral crystals. It is a very tough metal and can be hammered into a thin foil or drawn out into fine wire. It melts at 1086°C. , and, just below its melting point, is so brittle that it can be powdered. It can be vaporized in the electric arc, and its vapour has a bright green colour. When red hot Copper is allowed to cool slowly, it is quite brittle, but rapid cooling makes it soft, malleable and ductile (cp. Steel).

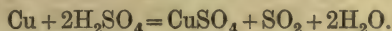
Copper is not acted on by dry air, but in the presence of moisture and Carbon Dioxide a green coating, called *Verdigris*, appears on its surface; this is a basic Carbonate of Copper.

Strong boiling Hydrochloric acid dissolves powdered Copper slowly, forming Cuprous Chloride and giving off Hydrogen gas:

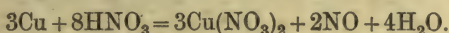


Dilute Sulphuric acid has no action on the metal, but the hot concentrated acid dissolves it, forming principally Copper

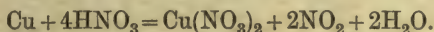
Sulphate and Sulphur Dioxide, with a varying amount of reduction products in the form of Sulphides of Copper :



Nitric acid dissolves Copper very readily, forming Copper Nitrate and evolving Oxides of Nitrogen. With a weak acid Nitric Oxide is the principal gas evolved :



With stronger acids, red Nitrogen Peroxide is given off :



Uses. Copper is one of the most useful of metals. On account of its high electrical conductivity, enormous quantities are used in the electrical industries. Because of its tough nature and the fact that water and air have little action upon it, it is largely used for kitchen utensils, kettles and boilers. It is also used for sheathing ships' bottoms.

It is the chief ingredient of many important alloys.

Brass consists of 2 parts of Copper to 1 of Zinc.

Bronze has about 80 per cent. of Copper and the remaining 20 per cent. consists of varying proportions of Tin and Zinc.

Nickel Silver, which is used for coins in Germany and the United States, contains about 75 per cent. of Copper and 25 per cent. of Nickel.

Gun-metal has 90 per cent. Copper and 10 per cent. Tin.

Speculum metal, which is used for large reflectors in optical instruments, consists of 2 parts of Copper to 1 of Tin.

Bell-metal has 3 of Copper to 1 of Zinc.

German Silver contains 60 per cent. Copper, 20 per cent. Zinc and 20 per cent. Nickel. It is used for making electrical resistance coils owing to its low conductivity.

COMPOUNDS OF COPPER.

Copper forms two series of salts—Cuprous and Cupric—derived from its two Oxides, Cuprous Oxide, Cu_2O , and Cupric Oxide, CuO .

Cuprous Oxide Cu_2O occurs native as Cuprite. It can be made by passing a current of air over finely-divided Copper which is gently heated.

It is also formed as a bright red precipitate when alkaline solutions of Cupric salts are reduced by weak reducing agents, such as grape sugar (p. 413).

Cuprous Oxide is insoluble in water, but is converted into Cuprous Chloride by strong Hydrochloric acid. Both Nitric and Sulphuric acids oxidize it, forming the Cupric salts of these acids.

It has a fine stable red colour and is used for paints and also to impart a rich ruby-red colour to glass.

Cuprous Chloride Cu_2Cl_2 is made by dissolving Cuprous Oxide in Hydrochloric acid or by acting upon Cupric Chloride and Copper turnings with Hydrochloric acid, when the nascent Hydrogen reduces the Cupric salt. When a solution thus obtained is poured into water, a white crystalline precipitate of Cuprous Chloride is thrown down.

Cuprous Chloride dissolves in Hydrochloric acid and in Ammonia, but these solutions gradually oxidize in the presence of air; they also absorb Carbon Monoxide and Acetylene gases if brought into contact with them.

Other Cuprous salts such as the Bromide, Iodide and Fluoride are known, but they are all unstable bodies.

In solution mono-cuprion Cu^+ —the ion of Cuprous salts—is colourless, whilst di-cuprion Cu^{++} —the ion of Cupric salts—possesses a blue colour.

Cupric Oxide CuO is formed when metallic Copper is strongly heated in a current of air, or by the action of gentle heat on the Carbonate, Nitrate or Hydroxide of Copper.

It is a black powder, which is hygroscopic and absorbs moisture from the air. At a high temperature it gradually changes into Cuprous Oxide.

Cupric Oxide readily gives up its Oxygen in the presence of reducing agents—Hydrogen, Carbon Monoxide, Hydrocarbons, etc.—and is used for the oxidation of substances in organic analyses.

When a small quantity of an alkali is added to the solution of a Cupric salt, a pale blue precipitate of Cupric Hydroxide

$\text{Cu}(\text{OH})_2$ is precipitated. On boiling strongly this is converted into black Copper Oxide. The blue Hydroxide dissolves in excess of alkali forming a deep blue solution. This solution possesses the power of dissolving Cellulose (cotton-wool, filter paper, etc.).

Cupric Chloride CuCl_2 is obtained by dissolving Cupric Oxide, or Carbonate, in Hydrochloric acid. When such a solution is evaporated to dryness, a brown deliquescent powder is obtained. Green crystals of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ can be obtained from solutions of the salt; such solutions are green when concentrated and blue if dilute.

Cupric Sulphate CuSO_4 is best obtained by dissolving Cupric Oxide in Sulphuric acid. It can be obtained from the solution in the form of blue triclinic crystals $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which are often called *blue vitriol*. When these crystals are heated to 100°C ., a pale blue substance $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is obtained, and at 240°C . the mass becomes white, forming *anhydrous Copper Sulphate*. This latter substance readily takes up water again, forming the blue crystals, and so is used as a test for the presence of water.

Like all soluble Copper salts, Cupric Sulphate is poisonous; it is used in solution as a germicide, for spraying wheat, potatoes and grape vines. It is also used in Daniell cells and for electro-plating.

Copper Sulphides. There are two Sulphides of Copper corresponding to the two Oxides—*Cuprous Sulphide*, Cu_2S , is formed as a grey crystalline substance when Copper burns in Sulphur vapour. *Cupric Sulphide*, CuS , is thrown down as a black precipitate when Sulphuretted Hydrogen is passed through solutions of Cupric salts.

Detection of Copper. Copper salts, when heated on charcoal with a reducing agent such as Potassium Cyanide, yield a red mass of metallic Copper.

Salts of Copper colour a bunsen flame green when introduced on a Platinum wire, with a flash of blue when the wire is first put in the flame.

Solutions of Copper salts give a black precipitate of Copper Sulphide, CuS , with Sulphuretted Hydrogen and a chocolate-

coloured precipitate of Copper Ferrocyanide, $\text{Cu}_2\text{Fe}(\text{CN})_6$, with Potassium Ferrocyanide. With excess of Ammonia a characteristic deep-blue solution is obtained with all soluble salts of Copper.

SILVER.

Symbol, Ag (Argentum). Atomic Weight, 107.9.

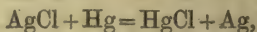
History. Silver has been known from very early times. It is mentioned in the Old Testament, and was used for coinage as early as Gold. The Phoenicians obtained the metal from Armenia and Spain. From the silvery colour of moonlight, the term Luna or Diana was used for Silver by early chemists.

Occurrence. Silver is found native occasionally in comparatively large masses. The principal ores of Silver contain its Sulphide, Ag_2S . This compound is found pure in *Argentite* and mixed with the Sulphides of Arsenic and Antimony in the ores *Proustite* and *Pyrargyrite*. Horn Silver or *Kerargyrite* consists of Silver Chloride, AgCl .

Silver is principally found associated with Lead in the mineral *Galena*, and most of the Silver in commerce comes from this source.

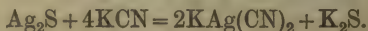
Extraction. Silver is extracted from its ores by many different processes, two of which will be considered here.

Amalgamation Process. In this process the ore is mixed with Common Salt which, in a day or so, changes it into Silver Chloride. Mercury is then added, which first replaces the Silver in the Chloride, thus :



and then forms an amalgam with the reduced Silver. This amalgam is heated, Silver remains behind and the Mercury which distils off is condensed and used again. This process has been used in Mexico and South America for over 300 years.

Cyanide Process. In this process, the crushed ores are mixed with a solution of Potassium or Sodium Cyanide. A double Cyanide of Potassium and Silver is formed thus :



This soluble double Cyanide is then treated with metallic Zinc, which replaces the Silver, going into solution as Zinc Cyanide, whilst the Silver is precipitated.

Desilverization of Lead. Lead, as prepared from Galena, usually contains varying amounts, up to 1 per cent., of Silver. Two processes are used for its extraction.

Pattinson's Process. This process, which is now dying out, depends upon the fact that, when a molten Silver-Lead alloy solidifies, the crystals of Lead, which first separate out, contain less Silver than the original alloy, and the remaining liquid is therefore enriched in Silver. About seven-eighths of the alloy is taken out with a perforated ladle, and both fractions are treated again in the same way. Ultimately an alloy containing $2\frac{1}{2}$ per cent. of Silver is obtained, and this is subjected to the process of *cupellation*. The alloy is melted in a cupel or test, in a reverberatory furnace, and blasts of hot air are played on its surface, the Lead is oxidized to Litharge and in the end a lump of pure Silver is left behind.

Parke's Process. In this process, argentiferous Lead is melted and a certain amount of Zinc is stirred into the liquid. The Zinc forms alloys of varying composition with the Silver, which alloys, being lighter than the Lead, rise to the surface. The molten mass is allowed to cool, and the Zinc-Silver alloys, having a higher melting point than Lead, solidify first and are skimmed off with a ladle. The alloy is next subjected to the process of *liquation* on a sloping surface; the more easily melted Lead runs away from the alloy and the remainder is next distilled. Zinc goes off as vapour, and Silver, with any Gold which may be present, is left behind and may be further purified by cupellation.

Properties. Silver is a bright white lustrous metal. In very thin sheets it appears blue by transmitted light.

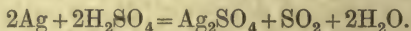
Pure air has no action upon it, but traces of Sulphuretted Hydrogen cause a black film of Silver Sulphide to form on its surface. Silver is very malleable and ductile; sheets only .00001 inch in thickness have been made. It has the highest conductivity for electricity and heat of all the metals.

Silver melts at 960° , and can be distilled in an electric furnace; Silver vapour has a greenish colour.

Molten Silver absorbs more than twenty times its volume of Oxygen, but gives up all but a very minute portion of it when it solidifies. The gas rises to the surface as bubbles, causing the phenomenon which is known as the "spitting" of Silver.

Both dilute and strong Nitric acid dissolve Silver readily, forming Silver Nitrate and evolving Oxides of Nitrogen.

Hydrochloric acid and dilute Sulphuric acid have no action on the metal, but boiling concentrated Sulphuric acid converts it into Silver Sulphate, Sulphur Dioxide gas being evolved:



Alloys. Sterling Silver, which is used for coinage, contains 92.5 per cent. of Silver and 7.5 per cent. of Copper. When sterling Silver is heated for some time in air, the Copper oxidizes, forming a thin film of Copper Oxide; if this film is dissolved away by dilute Sulphuric acid, a partially roughened surface of pure Silver is left. The substance thus formed is termed "frosted Silver." "Oxidized Silver" is made by dipping the metal into a solution of Sodium Sulphide, by which means a thin coating of black Silver Sulphide is formed on its surface.

COMPOUNDS OF SILVER.

Argentous Oxide Ag_2O is obtained, partially hydrated to AgOH , when Caustic Potash is added to a solution of Silver Nitrate. The hydrated Oxide forms a brown precipitate, which yields a black amorphous powder of Ag_2O on drying.

Silver Oxide is not a very stable compound and begins to give off its Oxygen when heated to 250°C . It is therefore a powerful oxidizing agent. It is only very slightly soluble in water (1 part in 3000), but the solution has a distinct metallic taste and alkaline reaction.

Silver Chloride AgCl is formed as a white curdy precipitate when any soluble Chloride is added to a solution of Silver Nitrate. This precipitate is insoluble in acids, but dissolves

readily in Ammonia or Potassium Cyanide, with which latter substance it forms a double Cyanide, $\text{KCN} \cdot \text{AgCN}$.

Silver Bromide AgBr and Silver Iodide AgI are formed in a precisely similar fashion to Silver Chloride. They are both yellow powders with similar properties to those of the Chloride.

Silver Nitrate AgNO_3 is prepared by dissolving Silver in Nitric acid. It forms colourless rhombic plate-like crystals which are very soluble in water. When the crystals are melted and allowed to solidify, a white crystalline mass is formed, used by doctors under the name of "*lunar caustic*."

Solutions of Silver Nitrate blacken, with the formation of metallic Silver, on exposure to light, when in contact with organic matter of any kind. Hence such a solution stains the skin and is also used as an indelible ink for marking linen.

Photography. All salts of Silver blacken, on exposure to light for some time, owing to their being reduced to metallic Silver. Even if only momentarily exposed to the influence of light, the parts exposed are rendered much more sensitive to the action of reducing agents than the unexposed parts. This property is made use of in photography.

A photographic plate or film has a thin coating of gelatine in which is suspended either Silver Chloride, Bromide or Iodide. No visible change is seen on the plate after exposure, but on treating it with suitable reducing agents, such as Ferrous Sulphate, Pyrogallie acid or Hydroquinone, the reduction process started by the light is carried on. Silver is formed by the reduction, the depth of the black deposit depending on the intensity of the light, to which that part of the film was subjected.

This process is called "developing" the film, and when the reduction is sufficiently far advanced, the unreduced Silver salt is dissolved away by immersion in a solution of Sodium Hyposulphite. This latter process is called "fixing," and the result is a "negative," in which the high lights of the original subject are dark and the darker parts transparent.

A "positive" print is taken from the negative by allowing light to pass through it on to a sensitive film very similar in

composition to the original film, which is developed in the same way.

Where what is known as Printing-out Paper (P.O.P) is used for the positive, the resultant print is "toned" before fixing. This consists in immersing the print in a solution containing Gold Chloride and Borax (or some similar feeble reducing agent), the Gold replaces the deposited Silver, forming a more permanent record of the exposure. In Platinotypes, the metal Platinum is used as a substitute for Gold.

Detection of Silver. Silver salts, when reduced on charcoal, give a white malleable bead of metallic Silver, which does not mark paper.

Solutions of Silver salts give a white curdy precipitate with Hydrochloric acid (or a soluble Chloride); this precipitate consists of Silver Chloride, AgCl , and is soluble in Ammonia; they also give a red-brown precipitate of Silver Chromate, AgCrO_4 , when Potassium Chromate is added.

GOLD.

Symbol, Au (Aurum). Atomic Weight, 197.2.

History. Gold, on account of its beautiful colour and unchangeable nature, was one of the first metals to attract the notice of man. Flint daggers with gilt handles have been excavated in Egypt, and the Gold mines of Nubia were worked extensively by the Egyptians. All the ancient kings and queens of Biblical history laid great store by this metal. The early chemists represented Gold by the symbol of the sun, not so much because of its appearance, but because it appeared to them the most noble of metals.

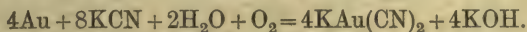
Occurrence. Gold is nearly always found native in nature. It occurs mostly in veins in quartz rock or in grains in alluvial gravels which are the products of the disintegration of quartz rock. It is also found in minute quantities in other substances. Sea water, for instance, contains 3.5 grains per ton, and Granites, Sandstones and Limestones have still more minute quantities disseminated through their masses. The chief localities where the metal is found are the Witwatersrand in

South Africa, Alaska in North America, Australia, India, etc.

Extraction. Gold is extracted from auriferous gravels by a purely mechanical process. The sand containing the Gold is placed in long narrow troughs and subjected to a strong stream of water. The lighter sand, etc., is swept away by the stream, but the specifically heavier Gold remains behind.

Gold-bearing quartz is first ground to a fine powder by hydraulic stamps and then, mixed with water, is allowed to flow as a slime over Copper plates amalgamated with Mercury. The Gold forms an amalgam with the Mercury, and this is afterwards distilled, the Mercury being driven off as vapour whilst the Gold remains behind.

Another process, the *Cyanide* process, consists in treating the powder from the stamps with a dilute solution of Potassium Cyanide in the presence of air. A double Cyanide of Potassium and Gold is formed and dissolves in the solution :



The Cyanide is treated with metallic Zinc, which precipitates the Gold, or else is subjected to electrolysis.

Gold is refined by electrolysis in a similar manner to metallic Copper (p. 402).

Properties. Gold is a yellow metal, but, if light is reflected several times from its surface before reaching the eye, it appears red. A thin film of Gold—Gold leaf—is green by transmitted light. It is the most malleable and ductile of metals, and sheets have been obtained which are only .000004 inch in thickness. It is not so good a conductor of electricity or heat as Silver or Copper.

It is not acted upon by Air, Oxygen or Steam at any temperature. It melts at a temperature of 1062°C. , and molten Gold is green in colour.

Gold is not affected by either Hydrochloric, Sulphuric or Nitric acids singly, but is dissolved by a mixture of Nitric and Hydrochloric acids, which is, for this reason, called *aqua regia* ; it dissolves the king of metals. The solution is really brought

about by the free Chlorine which is liberated when the acids are mixed.

When a dilute solution of Gold Chloride is made slightly alkaline by adding Magnesia and then subjected to the action of a reducing agent such as Formaldehyde or Hyposulphite of Soda, the Gold is precipitated in colloidal form, and the liquid becomes red in colour for that reason. The particles of Gold formed are so small that they do not settle under the action of gravity, and will pass through a filter paper unchanged.

If a mixture of Stannous and Stannic Chlorides is added to a very dilute solution of Gold Chloride, a precipitate of Hydrated Stannic Oxide is formed, and, at the same time, the Chloride of Gold is reduced to metallic Gold, which is deposited, as a thin layer, upon the grains of Stannic Oxide, causing it to assume a red or violet colour according to the strength of the solution. This precipitate has been known for a long time, and is called *Purple of Cassius*, after Cassius, who wrote about it as long ago as 1685. Similar deposits of Gold may be formed upon other substances, such as the Hydroxides of Calcium, Barium and Magnesium, on Aluminium Oxide or even China clay. Purple of Cassius is used for making the best ruby glass.

Gold is too soft a metal to be used alone, either for jewellery or coinage, so it is usually alloyed with Copper, which makes it harder and redder in colour. English Gold coins contain 96.17 per cent. of Gold and the rest is Copper.

The amount of Gold in a Copper-Gold alloy is usually expressed in *carats*, 24 carat Gold being absolutely pure Gold; so that 18 carat Gold is an alloy containing 18 parts of Gold out of 24 of alloy.

The quantity of Gold present in an alloy with Copper is determined, without much injury to the object of the experiment, by making a *streak* with it upon a hard white surface, such as unglazed earthenware, and treating the streak with dilute Nitric acid; from the depth of the green colouration produced, due to the formation of Copper Nitrate, the quantity of Copper present can be calculated by comparing its colour with that produced by alloys of known composition.

COMPOUNDS OF GOLD.

The compounds of Gold are not of any great importance ; most of them are unstable bodies, and are at once reduced to Gold by the application of heat.

Auric Chloride AuCl_3 is made by the action of Chlorine or of *aqua regia* upon Gold. It occurs in reddish-yellow crystals, which are soluble in water. On heating it is first reduced to Aurous Chloride, AuCl , and then to metallic Gold.

It is used for the toning of Silver prints in photography. When a solution of Gold in *aqua regia* is treated with Ammonia and the precipitate formed is dissolved by a solution of Potassium Cyanide, the solution contains Potassium Auricyanide, $\text{KAu}(\text{CN})_2$, and is largely used for electro-gilding.

Detection of Gold. Gold is always detected in its solutions by reducing them to metallic Gold with the aid of suitable reducing agents. Thus, Sulphurous acid or Ferrous Sulphate solution give, on warming for a little time, a black precipitate of finely-divided Gold, whilst a mixture of Stannous Chloride with a little Stannic Chloride produces the precipitate, Purple of Cassius, described above.

PROBLEMS.

75. An electric current passed through a solution of Copper Sulphate caused the evolution of 60 c.c. (measured at 12°C . and 760 mm.) of Oxygen gas at the anode, and the deposition of .3261 gram of Copper at the cathode. The Specific Heat of Copper is .095. Calculate from these data the Atomic Weight of Copper. (Camb. Univ. Schol. Exam.)

76. Calculate the equivalent weight of Gold from the following data : 100 c.c. of Hydrogen (measured at 0°C . and 760 mm.) were evolved by the action of dilute Sulphuric acid on some Zinc. Using the same quantities of Zinc and Sulphuric acid, but adding some Gold Chloride solution to the liquid, it was found that only 44.5 c.c. of Hydrogen (at 0°C . and 760 mm.) was obtained, and .3258 gram of Gold was deposited.

PRACTICAL EXERCISES.

To prepare Cuprous Oxide. Take about 30 c.c. of a solution of Copper Sulphate in a beaker, add 2 or 3 grams of Rochelle

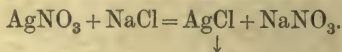
Salts (Sodium Potassium Tartrate), warm till it is dissolved, and then add excess of Caustic Soda solution. The effect of the Rochelle Salts is to prevent the precipitation of Cupric Hydrate which remains in the solution.

Now add one or two grams of Grape Sugar, and warm gently ; the Sugar acts as a reducing agent on the Cupric Hydrate, forming Cuprous Oxide, which, being insoluble in water, is thrown down as a bright red precipitate.

Filter the liquid and dry the Cuprous Oxide on the filter paper.

Experiments on the Volumetric estimation of Silver.

The volumetric estimation of Silver depends upon the fact that all soluble salts of Silver yield a white precipitate of Silver Chloride when a solution of common Salt is added to the liquid. With Silver Nitrate the equation is :



From this equation it is seen that 108 grams of Silver are exactly precipitated by 58.5 grams of Sodium Chloride.

To prepare a Standard $\left(\frac{N}{10}\right)$ solution of Salt. Weigh out accurately 5.85 grams of *pure* Sodium Chloride. Place in a litre flask, dissolve it in distilled water and fill up to the mark.

Each c.c. of this solution contains .00585 gram of Sodium Chloride, and is consequently equivalent to .0108 gram of metallic Silver.

To find the percentage of Silver in Silver Nitrate. Weigh out 1 gram of Silver Nitrate, dissolve it in distilled water and make the solution up to 100 c.c.

Place this solution in a "cleaned" burette, and take 25 c.c. of the $\frac{N}{10}$ Sodium Chloride solution in a porcelain dish. Add to the salt solution one or two drops of Potassic Chromate solution to serve as an indicator.

Add the Silver Nitrate solution to the liquid in the dish, stirring continuously, till, on the addition of one drop, a brown precipitate is formed with the Potassic Chromate, which cannot be stirred away.

Repeat the experiment to get a constant result ; then, from the number of c.c. of Silver Nitrate added, the weight of Silver in the solution can be calculated from the fact that each c.c. of the Sodium Chloride solution is equivalent to .0108 gram of Silver.

To find the percentage of Silver in a Silver Coin. Weigh out about .5 gram of the coin, dissolve in dilute Nitric acid, making the liquid, when the solution is complete, up to 100 c.c. with distilled water.

Since this liquid is acid, Potassic Chromate cannot be used as an indicator ; proceed as follows. Take 25 c.c. of the Silver Nitrate solution in a stoppered bottle, and add to it the

$\frac{N}{10}$ NaCl solution prepared as described above.

N.B.—During the titration the bottle must be wrapped up in a dark cloth to prevent the access of light.

After every addition of Sodium Chloride solution, shake the bottle vigorously, till the precipitate of Silver Chloride is clotted together. Then allow it to settle till the supernatant liquid is clear. Continue this procedure till one drop of the Sodium Chloride solution fails to produce turbidity in the supernatant liquid ; this marks the end of the reaction.

Make your calculation on the assumption that 1 c.c.

$\frac{N}{10}$ NaCl is equivalent to .0108 gram of Silver.

CHAPTER XXIX.

THE METALS OF THE ALKALINE EARTHS.

THE three elements Calcium, Strontium and Barium form a group of metals with well marked similarities both in their physical and chemical properties. They are called Alkaline Earths, because the Oxides obtained when their Carbonates or "Earths" are calcined have a strong alkaline reaction in solution.

All the three metals are fairly stable in air; they combine with water at ordinary temperatures with the evolution of Hydrogen gas. They are bi-valent in nearly all their compounds. The Oxides shew an increase in solubility with rise in Atomic Weight from Calcium (40) to Barium (137), and the Sulphates a corresponding decrease, Barium Sulphate being one of the most insoluble substances known. Their Carbonates are all insoluble and their Nitrates and Chlorides all soluble in water. In addition to a basic Oxide of general formula RO , they all form Peroxides with formula RO_2 .

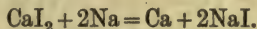
CALCIUM.

Symbol, Ca. Atomic Weight, 40.1.

Occurrence. Calcium is met with abundantly in combination, its principal compound being Calcium Carbonate, $CaCO_3$. This substance is found in masses as Limestone or Chalk, in crystals as *Calcite*, *Iceland Spar* or *Aragonite*, and is the principal constituent of most shells, from that of a large Crustacean to that of a minute Foraminifera. Calcium occurs

also as Sulphate in *Gypsum* or *Selenite*, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, as Fluoride in *Fluorspar*, CaF_2 , and in many volcanic rocks as Calcium Silicate. It is also found in bones as Calcium Phosphate, $\text{Ca}_3(\text{PO}_4)_2$.

Preparation. Metallic Calcium was a rarity till comparatively recently. Davy prepared some as long ago as 1808. Moissan (1898) obtained the metal by heating Calcium Iodide with metallic Sodium :

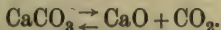


Nowadays, it is obtained on a fairly large scale by the electrolysis of molten Calcium Chloride.

Properties. Calcium is a silver-white metal, which tarnishes slowly in air. Its density is 1.85, and it melts at 780°C . When heated in air it burns, forming Calcium Oxide, CaO . If heated for some time in an atmosphere of Nitrogen, it gradually absorbs the gas, forming Calcium Nitride, Ca_3N_2 . Water attacks it comparatively slowly with the evolution of Hydrogen, but if a small quantity of acid is present, the action is violent.

COMPOUNDS OF CALCIUM.

Calcium Oxide, Lime, CaO . When Calcium Carbonate is heated strongly for some time, Carbonic acid gas is evolved and Calcium Oxide or Quicklime is left behind. Since, when Carbonic acid gas is led over cold Calcium Oxide, it is absorbed, forming Calcium Carbonate, the action is a reversible one, and should be written thus :



When the operation of heating the Calcium Carbonate is carried on in a closed Iron vessel, fitted with a pressure gauge and a thermometer, it is found that for every temperature there is a perfectly definite pressure of the Carbonic acid gas, and hence the three substances CaCO_3 , CaO and CO_2 must have reached a state of equilibrium, which means that, in a given time, exactly as many molecules of CaCO_3 dissociate into CaO and CO_2 as there are molecules of CaO and CO_2 associating

to form CaCO_3 . When the temperature is raised, more molecules dissociate than associate, until equilibrium is again attained with an increased pressure.

Limestone is calcined on a large scale for the production of Quicklime. Formerly stacks of Limestone were built in a kiln and heated, by fires from underneath, for upwards of a week. Latterly, a continuous process is used; a mixture of Limestone and good Coal is introduced at the top of the kiln (Fig. 146). The Coal takes fire about two-thirds of the way

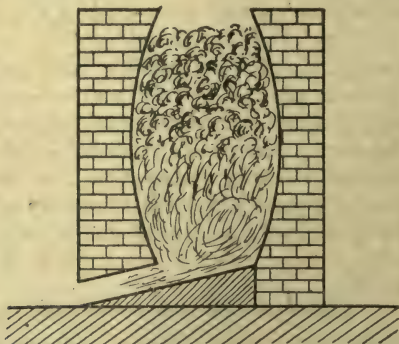


FIG. 146.—Section of a Lime Kiln. (Diagrammatic.)

down, and Lime, mixed with a small quantity of ash, which is not harmful from a commercial point of view, is taken out at the bottom of the kiln. —

Calcium Oxide is a white amorphous powder. It is a very refractory solid, and requires the high temperature of the electric furnace—about 3000°C .—to melt it. When made white hot in an Oxy-hydrogen flame, it gives out an intensely luminous light, used in lanterns under the name of *limelight*.

If a few drops of water are added to a lump of freshly “burnt,” though cold, Quicklime, a hissing sound, due to the formation of steam, is heard, a large quantity of heat is evolved, and the lump breaks up into a fine dry powder called *Slaked Lime*, or Calcium Hydroxide, $\text{Ca}(\text{OH})_2$.

Calcium Hydroxide dissolves sparingly in cold water and, contrary to the usual rule, is only half as soluble in boiling water. The solution is known as Lime Water, and is alkaline towards Litmus.

The extreme readiness with which Calcium Oxide absorbs water is made use of both in the laboratory and in the arts. For instance, it is used for drying gases and purifying Coal gas and for removing the hair from hides in the preliminary process of tanning. Lime is also used for making mortars and cements, in glass-making, and for a flux in metallurgical processes.

Mortar is a mixture of slaked Lime, Sand and water. It "sets" or hardens almost entirely by the simple action of drying, though the outer layers are usually changed into Calcium Carbonate by the Carbon Dioxide in the air. Roman walls after 2000 years' exposure have been found to have only a superficial layer of the Carbonate, the inside still consisting of Calcium Hydroxide and unaltered Sand.

When used as a cement for plastering, hair is mixed with the mortar to make it stick together.

If there is a little clay and sand in the limestone used for making Lime, the burnt substance sets into a hard mass when mixed with water, and this hard mass is capable of resisting the continuous action of water. It is called *hydraulic cement*, and is most useful for bridge foundations, etc.

Calcium Chloride CaCl_2 is made, as a bye-product, in several chemical manufactures. It is a highly deliquescent solid, and is much used in the laboratory for drying gases. It can be obtained in the form of crystals, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, which are extremely soluble in water—100 parts of water at 16° dissolve 400 parts of the salt. A saturated solution of this salt boils at 180°C .

A mixture of Calcium Chloride and Ice (or Snow) produces a very cold freezing mixture; a temperature of -40°C . can be obtained by this means.

Calcium Hypochlorite, Bleaching Powder. See page 188.

Calcium Sulphate CaSO_4 . This substance occurs in nature in the anhydrous form as *Anhydrite*, CaSO_4 , and, with two

molecules of Water of crystallization, as colourless crystals in *Selenite*, in white crystalline masses as *Gypsum* and in fine grained masses as *Alabaster*. All these three last-named minerals have a formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

When Gypsum is heated for some time to a temperature of 120°C ., it loses three-fourths of its Water, leaving a substance with the formula $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, but does not lose it all till a temperature of 200°C .

The partially dehydrated substance is called *Plaster of Paris*, and possesses the property of taking up Water again, when mixed with it, becoming quite hard and white. This most useful property is made use of in the taking of casts of all sorts of objects, in making plaster casts and in surgical bandages.

If the original Gypsum is heated so strongly as to lose all its Water, it will not take up any water again, and is said to be "dead burnt."

Calcium Carbonate CaCO_3 . The various forms of this compound found in nature have already been enumerated.

Calcite and Aragonite are dimorphous, *i.e.* they are the same chemical compound, crystallizing in two perfectly distinct crystalline forms. They can both be formed artificially from solutions of Calcium Carbonate; when cold, Calcite is deposited, and when hot, Aragonite crystals are obtained.

Calcium Carbonate is practically insoluble in pure water, but dissolves to a small extent—7 gram in 1000 grams of water—when the water is saturated with Carbon Dioxide, owing to the formation of Calcium Bicarbonate $\text{CaH}_2(\text{CO}_3)_2$. This latter substance decomposes when the solution is boiled.

French Chalk and Whitening consist mainly of Calcium Carbonate.

Calcium Carbide CaC_2 . This substance is made by subjecting a mixture of Quicklime and Coke to the high temperature of an electric furnace :



The process may be imitated, on a small scale, in the apparatus shewn in the diagram (Fig. 147). *A* is a graphite crucible, joined by a metal clamp to a retort stand, *B* is a carbon rod

similar to those used for arc lights, joined to another retort stand by a metal clamp; both retort stands are insulated by placing them on ebonite blocks *E, E*. An electric supply of about 100 volts is joined to the two stands as indicated. By means of the insulating handle *C*, the carbon rod is lowered into contact with the crucible and then raised to form an arc. The mixture is introduced in the proper proportions, and action takes place as stated above.

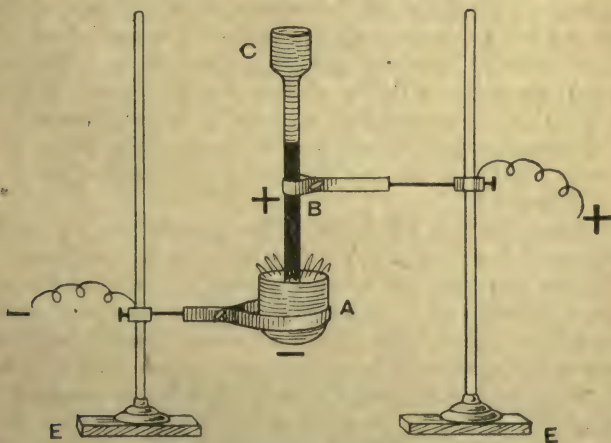
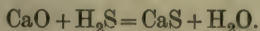


FIG. 147.—Preparation of Calcium Carbide.

Calcium Carbide is, when pure, a hard white brittle solid; the commercial substance is usually grey owing to impurities. Its chief use is for the production of Acetylene gas. It must be kept in air-tight tins, owing to the action of atmospheric moisture upon it.

Calcium Sulphide CaS can be made by passing Sulphuretted Hydrogen over heated Lime :



Its most interesting property is that it gives out a feeble light or phosphorescence in the dark, after being previously

exposed to a bright light. It gradually loses this property, but regains it on again subjecting it to a bright light. It is called Canton's Phosphorus, and the corresponding Barium Sulphide, which possesses similar properties, is called Bolognian Phosphorus. These Sulphides are used for making luminous paint.

Detection of Calcium. Salts of Calcium are recognized by the brick-red colour which they impart to the bunsen flame. Soluble Calcium salts also give white precipitates with both Ammonium Carbonate and Ammonium Oxalate.

Salts of Calcium are often very difficult to distinguish from Strontium salts, but they will give a white precipitate of Calcium Arsenite on the addition of a strong solution of Ammonium Arsenite in Ammonium Hydrate; salts of Strontium do not give this precipitate.

STRONTIUM.

Symbol, Sr. Atomic Weight, 87.6.

This metal is found in nature in two compounds *Strontianite*, Strontium Carbonate, SrCO_3 , and *Celestine*, Strontium Sulphate, SrSO_4 .

In its method of preparation and its properties, it is very similar to Calcium.

Its compounds are very similar to the corresponding Calcium compounds, and the Nitrate of Strontium is used largely for fireworks, owing to the intense red colour which it imparts to a flame.

Detection of Strontium. Salts of Strontium impart an intense crimson colour to a bunsen flame.

Soluble salts give white precipitates with Ammonium Carbonate and Ammonium Oxalate, and with Calcium Sulphate a white precipitate of Strontium Sulphate is formed, but this only occurs on standing for a little time or on boiling the liquid.

BARIUM.

Symbol, Ba. Atomic Weight, 137.4.

Occurrence. Barium is found in nature chiefly as its Carbonate, BaCO_3 , in *Witherite*, and as Sulphate, BaSO_4 , in *Barytes* or *Heavy Spar*.

The metal can be made by a similar process to that used for Calcium, but with much greater difficulty. It resembles Calcium in all its properties.

SALTS OF BARIUM.

Barium forms two Oxides, the Monoxide, BaO , and the Dioxide, BaO_2 .

Barium Monoxide, Baryta, BaO , is most readily obtained by the action of moderate heat on Barium Nitrate or intense heat on Barium Carbonate.

It is a strongly alkaline compound and, like Lime, slakes with water, evolving so much heat that the mass becomes red hot.

It is more soluble in water than Calcium Oxide.

When heated to a dull red heat in air or Oxygen, it takes up another atom of Oxygen, forming Barium Dioxide.

Barium Dioxide, Barium Peroxide, BaO_2 , is formed as indicated in the paragraph immediately above.

It is a grey powder, which evolves Oxygen at a bright red heat, and was formerly used for obtaining Oxygen, commercially, by Brin's process.

If gently warmed in a stream of Sulphur Dioxide, the two substances combine, forming Barium Sulphate, and the whole mass becomes incandescent.

Barium Nitrate $\text{Ba}(\text{NO}_3)_2$ is used in pyrotechny for the preparation of green fires.

All soluble Barium salts are poisonous.

Detection of Barium. Barium salts impart a yellowish-green colour to the bunsen flame.

Soluble salts of Barium give white precipitates with Sulphuric acid (or Calcium Sulphate), Ammonium Carbonate and

Ammonium Oxalate. They also give a yellow precipitate of Barium Chromate with Potassium Chromate; this precipitate is insoluble in Acetic acid, and in this respect it differs from the Chromates of Calcium and Strontium.

PROBLEMS.

77. 10 grams of a mixture of Chalk and Sand were treated with Hydrochloric acid. 1234 c.c. of Carbon Dioxide, measured at 15° C. and 750 mm., were evolved. Find the percentage composition of the mixture.

78. 1.25 grams of Barium Chloride crystals were dissolved in water and precipitated by dilute Sulphuric acid as Barium Sulphate. This latter substance, when dry, was found to weigh 1.195 grams. Find the percentage of Barium in the crystals of Barium Chloride, if the formula for Barium Sulphate is BaSO_4 .

CHAPTER XXX.

METALS OF THE ZINC GROUP.

THIS group consists of four metals—Beryllium, Magnesium, Zinc and Cadmium—which resemble one another closely in their properties and compounds.

For instance, they all tarnish very slowly in moist air, and have to be heated quite strongly before they take fire, forming their Oxides, which have a general formula RO .

They are unaffected by water at ordinary temperatures, but when steam is passed over the heated metal, it is decomposed and Hydrogen is liberated.

They are attacked by dilute Hydrochloric and Sulphuric acids, without any great violence, Hydrogen gas being evolved.

All four metals are di-valent in their compounds. Their Oxides are practically insoluble in water.

The Sulphates of Zinc and Magnesium both crystallize with seven molecules of Water, and are isomorphous.

Beryllium (Be, At. Wt. 9.1) is found principally in the mineral *Beryl*, which is a double Silicate of Beryllium and Aluminium; in a transparent form this mineral forms the *Emerald*.

Neither Beryllium nor its salts are of much importance.

MAGNESIUM.

Symbol, Mg. Atomic Weight, 24.3.

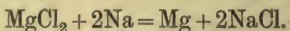
Occurrence. Magnesium is found always in the combined state, and principally as its Carbonate. This compound occurs as the mineral *Magnesite*, $MgCO_3$, and, in combination

with Calcium Carbonate, it occurs both in crystals and rock masses as *Dolomite*, $(\text{MgCa})\text{CO}_3$.

Magnesium is also found as Chloride in *Carnallite*, $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$, and as Silicate, mixed with the Silicates of other metals, in *Asbestos*, *Talc*, *Serpentine* and *Olivine*.

Preparation. Magnesium is made, in considerable quantities, by the electrolysis of fused Magnesium Chloride or Carnallite. The metal, being lighter than the fused salt, rises to the surface, and care is taken to prevent access of air and the consequent oxidation of the molten Magnesium.

It used formerly to be prepared by heating a mixture of Magnesium Chloride and metallic Sodium in a crucible raised to a bright red heat :



Properties. Magnesium is a silvery-white metal, unaffected by dry air, but in moist air it acquires a white tarnish, which consists of Magnesium Oxide.

It melts at 632°C . and boils at about 1100°C .

When heated strongly in air, especially if in the form of powder, it takes fire, burning with a brilliant dazzling white flame, which is very rich in the ultra blue or chemically active rays, and so is used for photographic purposes. The "flash light" for this purpose is made by blowing Magnesium powder through a flame of Methylated Spirits.

Boiling water attacks Magnesium very slowly, but when Steam is passed over the heated metal, it is decomposed.

Magnesium dissolves readily in dilute Hydrochloric and Sulphuric acids, evolving Hydrogen, and is almost the only metal which will yield Hydrogen gas when acted upon by Nitric acid.

It is unacted upon by boiling solutions of the Caustic Alkalies (cp. Zinc).

Magnesium is one of the few metals which will combine directly with Nitrogen; it forms Magnesium Nitride, Mg_3N_2 .

Magnesium is used for photographic purposes, in fireworks, and it forms an alloy with Aluminium, called *Magnalium*,

which, being light and strong, is used for the beams and scale-pans of balances.

COMPOUNDS OF MAGNESIUM.

Magnesium Oxide, Magnesia, MgO , is formed when the metal burns in air, or when the Nitrate or Carbonate of the metal is ignited strongly. Commercial Magnesia known as *Calcined Magnesia* or *Magnesia usta* is made from the Carbonate.

Magnesium Oxide is a white powder, very slightly soluble in water—1 part in 100,000—but the solution is sufficient to give a slightly alkaline reaction with litmus.

It is highly refractory, melting at about $2000^{\circ}C$., and on this account it is used as a substitute for Lime in producing "Lime-light"; also for making crucibles and furnace bricks.

All the salts of Magnesium can be obtained by dissolving Magnesia in the proper acid.

Magnesium Sulphate, Epsom Salts, $MgSO_4 \cdot 7H_2O$, is found dissolved in the water of many mineral springs, and also, in nature, as the mineral *Kieserite*, $MgSO_4 \cdot H_2O$. It forms needle-shaped, rhombic crystals, which are isomorphous with Zinc Sulphate; these crystals lose 6 molecules of water at $150^{\circ}C$., but retain the seventh till a temperature of $200^{\circ}C$. is reached.

It forms, with the alkaline Sulphates, a series of isomorphous double Sulphates with the general formula, $MgSO_4 \cdot R_2SO_4 \cdot 6H_2O$.

It is used as a medicine (usually called simply "Salts") and in the dyeing and tanning industries.

Detection of Magnesium. When Magnesium salts are heated strongly on charcoal, a white infusible residue of Magnesium Oxide is left; this residue, if moistened with a few drops of Cobalt Nitrate and reheated, turns pink.

Soluble Magnesium salts give, in the presence of Ammonium salts, a white crystalline precipitate with Sodium Hydrogen Phosphate; this precipitate has a composition of NH_4MgPO_4 .

With Ammonium Hydrate, a white precipitate of $\text{Mg}(\text{OH})_2$ is formed, and with Ammonium Carbonate a white precipitate of $\text{Mg}(\text{OH})_2 \cdot \text{MgCO}_3$, but neither of these precipitates forms in the presence of Ammonium Chloride.

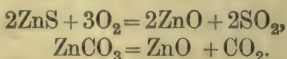
ZINC.

Symbol, Zn. Atomic Weight, 65.4.

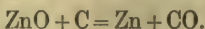
Occurrence. The two principal ores of Zinc are the Sulphide, *Zinc Blende* or *Black Jack*, ZnS , and the Carbonate, *Calamine*, ZnCO_3 . It is also met with in *Zincite*, ZnO , *Willemite*, $2\text{ZnO} \cdot \text{SiO}_2$ and *Zinc Spinel* or *Gahnite*, $\text{ZnO} \cdot \text{Al}_2\text{O}_3$.

Preparation. The extraction of Zinc from its ores is performed in two stages.

(1) The ore is changed into Oxide. This is done in the case of Blende by *roasting* in a current of air, and in the case of Calamine by *calcining* the ore. The reactions which occur are given by the equations :



(2) The Oxide is reduced by mixing it with coke and heating the mixture strongly; the Zinc distils off as vapour, which is condensed :



The retort in which the heating is conducted and the method by which the Zinc is condensed vary in the different processes. The Belgian retort and receiver is shewn in the diagram (Fig. 148). Twenty or thirty of these are heated in a furnace at the same time; the nozzles and condensers being on the outside, are cooled by the air.

Commercial Zinc is always impure, the chief impurities being Carbon, Iron, Arsenic and Cadmium. It may be purified to a considerable extent by re-distillation, but this does not get rid of the Arsenic.

Properties. Zinc is a bluish-white metal, very crystalline and brittle. At temperatures between 100°C . and 150°C .,

it becomes malleable and can be rolled into sheets, but above 200° C. it again becomes so brittle that it can be powdered.

Zinc is acted upon slowly by moist air, acquiring a white tarnish. It melts at 420° C. and, at a higher temperature, takes fire in air, burning with a bright bluish flame, leaving behind Zinc Oxide in the form of a white flocculent substance, like wool, and formerly known as *philosopher's wool*.

Pure Zinc is almost unacted on by dilute

Hydrochloric or Sulphuric acids, but the presence of a very small quantity of impurity causes the metal to dissolve rapidly with the evolution of Hydrogen gas. Strong boiling Sulphuric acid attacks Zinc, forming the Sulphate and giving off Sulphur Dioxide gas :

$$\text{Zn} + 2\text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}.$$

Nitric acid dissolves Zinc readily, forming Zinc Nitrate and evolving Oxides of Nitrogen or even Ammonia gas, according to the strength of the acid.

Caustic alkalis dissolve Zinc readily with the evolution of Hydrogen.

Zinc is largely used for *galvanizing* Iron. A thin layer of Zinc is formed on the Iron, either by dipping very clean sheet Iron into molten Zinc or by depositing Zinc electrolytically upon the Iron. Such galvanized Iron is able to withstand the effects of air and water, and is used for wire netting, corrugated roofing-sheets and water tanks.

Zinc is an important constituent of many alloys, the chief of which are *Brass*, *German Silver* and *Bronze* (see Copper, p. 403).

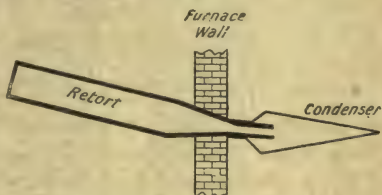


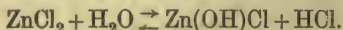
FIG. 148.—Belgian Zinc retort.

COMPOUNDS OF ZINC.

Zinc Oxide ZnO is formed by heating metallic Zinc in a current of air and condensing the fumes evolved. It is known commercially as *Zinc White*, and is used, instead of White Lead,

in paints, as it is non-poisonous and does not blacken with Sulphuretted Hydrogen. It possesses the peculiar property of becoming yellow when heated, but regains its original pure white colour on cooling.

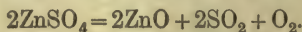
Zinc Chloride ZnCl_2 can be made by the direct action of Chlorine on Zinc or by dissolving the metal in Hydrochloric acid. When this latter solution is evaporated, a certain amount of "hydrolysis" occurs, resulting in the production of Hydrochloric acid and either Zinc Oxide or a basic Chloride of Zinc, $\text{Zn}(\text{OH})\text{Cl}$:



A similar reaction occurs with Magnesium Chloride.

In these reactions hydrolysis is seen to be the reverse of neutralization, as the salt is separated partially into free acid and base.

Zinc Sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is made by dissolving Zinc in dilute Sulphuric acid. It is commonly known as *White Vitriol*. It loses 6 of its molecules of Water at 100°C ., but retains the last molecule till 300°C . At a white heat it is completely decomposed into Zinc Oxide, Sulphur Dioxide and Oxygen :



Zinc Sulphate, like all soluble salts of the metal, is poisonous.

Detection of Zinc. When compounds of Zinc are heated on charcoal, a white infusible residue of Zinc Oxide remains ; this, if treated with a few drops of Cobalt Nitrate and reheated, acquires a green colour.

Soluble Zinc salts give a white precipitate of Zinc Sulphide with Ammonium Sulphide in alkaline solutions ; they also form white precipitates with both Caustic Soda and Potassium Ferro-cyanide.

CADMIUM.

Symbol, Cd. Atomic Weight, 112.4.

Cadmium is nearly always present in all Zinc ores ; it occurs also as Sulphide in the rare mineral *Greenockite*, CdS .

It resembles Zinc both in its properties (it is rather more malleable than Zinc), its mode of preparation and its com-

pounds. It is, however, not attacked by Caustic alkalies as is Zinc.

It is detected by the characteristic brown colour of Cadmium Oxide, which is formed when any of its salts are heated on charcoal.

Soluble Cadmium salts give a yellow precipitate with Sulphuretted Hydrogen, which is not dissolved by Caustic Soda, and is therefore readily distinguished from the similarly coloured Arsenic Sulphide.

PROBLEMS.

79. .5 gram of Magnesium was completely converted into its Oxide and the Oxide exactly neutralized 20 c.c. of a solution of Sulphuric acid. Find the strength of the acid solution in grams per litre.

80. A piece of Zinc weighing 5 grams was placed in 100 c.c. of N. HCl. When action ceased, the Zinc was taken out and dried, and its weight was found to be 1.75 grams. Calculate the equivalent of Zinc.

81. A specimen of Zinc having Zinc Oxide as its only impurity, weighed .72 gram. When placed in dilute acid, 250 c.c. of Hydrogen (measured at 12° C. and 745 mm.) were evolved. Find the percentage of pure Zinc in the mixture.

CHAPTER XXXI.

MERCURY AND ITS COMPOUNDS.

THE element Mercury is found in the column of Group II. of the Periodic Law Table (p. 137), and possesses certain points of resemblance to the elements Zinc and Cadmium, which occur in the same Group, but in most respects it differs widely from these metals, nor does it shew any great likeness to any other element. It is best studied by itself.

It resembles Zinc and Cadmium in that in its chief series of salts Mercury is di-valent, but it forms a well-marked series of salts, in which it exhibits mono-valency, to which neither Zinc nor Cadmium shew the least tendency. In these mono-valent salts Mercury rather resembles Silver—the Chlorides being insoluble white substances, etc.

Again, the Oxides and Hydroxides of Zinc, Cadmium and Mercury are insoluble in water, as are their Carbonates and Sulphides. On the other hand, Mercuric Sulphide and Cadmium Sulphide are insoluble in Hydrochloric acid, but the Sulphide of Zinc dissolves readily in this reagent.

The Chlorides of all three metals are soluble in water, but Zinc Chloride is very deliquescent. Mercuric Chloride is not at all deliquescent, and only sparingly soluble.

MERCURY.

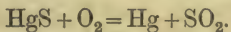
Symbol, Hg (Hydrargyrum). Atomic Weight, 200.0.

History. Mercury, or Quicksilver, as it is often called, was known to the old Greek chemists. From its appearance they

named it Hydrargyrum (Water Silver), and the English name Quicksilver (live Silver) is another expression of the same thing. Its name of Mercury was derived from Hermes or Mercury, the messenger of the Gods.

Occurrence. Mercury occurs free in very small quantities, and its only ore of any importance is *Cinnabar*, Mercuric Sulphide, HgS . This is worked at Almaden (Spain), in Austria, Bavaria, China and other places.

Preparation. Mercury is obtained from Cinnabar by roasting the ore in a strong current of air. The Sulphur is oxidized to Sulphur Dioxide, and passes off with the Mercury vapour :



The Mercury vapours are condensed either in a series of brick-work chambers or by passing them through a series of pear-shaped earthenware vessels—called *aludels* (Fig. 149), which fit one into the other and are cooled by the atmosphère. The crude



FIG. 149.—Aludels.

Mercury is purified by distillation or by allowing it to run through dilute Nitric acid, which dissolves out the impurities.

Properties. Mercury, at ordinary temperatures, is a bright silvery liquid. It forms a malleable solid when cooled to -39°C ., and boils at 357°C ., forming a colourless vapour.

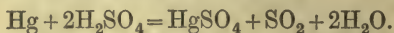
The density of this vapour is approximately 100 ($H=1$), and as the accepted value for the atomic weight of Mercury is 200, this vapour must contain monatomic molecules. In this property it resembles the elements Zinc and Cadmium.

Mercury is unacted upon by air at ordinary temperatures, but, at its boiling point, it combines with Oxygen, forming red Mercuric Oxide.

Most of the gases which are prepared in the laboratory have no action upon Mercury ; hence the liquid is used for collecting such gases as are soluble in water.

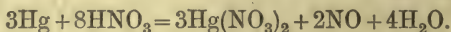
Hydrochloric acid has no action on Mercury, but boiling

strong Sulphuric acid dissolves the metal, forming Mercuric Sulphate and evolving Sulphur Dioxide :



Priestley first prepared Sulphur Dioxide by this method.

Nitric acid acts upon Mercury in a precisely similar manner to Copper, *i.e.* a strong acid gives Mercuric Nitrate and Nitrogen Peroxide (NO_2); a weaker acid evolves Nitric Oxide, thus :



The Caustic Alkalies have no action on Mercury.

Alloys of Mercury. Mercury forms alloys with nearly all the metals. They are, in a way, solutions of the metals in Mercury and are called *Amalgams*. In some cases, as, for example, with Sodium and Potassium, the formation of the amalgam is attended by evolution of heat, in others, as in Tin amalgam, heat is absorbed.

The amalgams of the Alkali metals act upon water in the same manner as the metals themselves, but with much less violence. They are used for making nascent Hydrogen in a solution where an acid cannot be used.

Zinc amalgam is acted upon very slowly by dilute Sulphuric acid; hence the Zinc plates of electric batteries are coated with this amalgam to prevent their wasting away when the current is not being used.

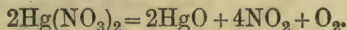
Tin amalgam, which is very soft, is used for the reflecting surface of ordinary mirrors. Amalgams of Gold, Zinc and Copper are used by dentists for stopping teeth; they are soft when first made, but become quite hard after a while, and are practically unaffected by the saliva and other liquids in the mouth.

COMPOUNDS OF MERCURY.

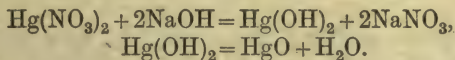
Mercury forms two Oxides, Mercurous Oxide, Hg_2O and Mercuric Oxide, HgO , and derived from them are two well-marked series of salts, the mono-valent Mercurous (Hg') salts and the di-valent Mercuric (Hg'') salts.

Mercurous Oxide Hg_2O is an unstable dark-brown powder, which, when gently heated or exposed to light, decomposes into Mercury and Mercuric Oxide.

Mercuric Oxide HgO is formed when Mercury is kept, for a considerable time, near its boiling point in air, but is more readily obtained by heating Mercuric Nitrate :



As thus obtained, it is a bright-red crystalline powder, but it may also be obtained as a yellow precipitate by adding Caustic Soda to a solution of any Mercuric salt and heating the Mercuric Hydrate, which is thrown down, to a temperature of $150^\circ \text{C}.$:

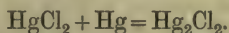


The two powders are most probably alike, the difference in colour being due to a finer state of subdivision in the yellow form.

When heated, Mercuric Oxide becomes nearly black in colour, and is completely decomposed into Mercury and Oxygen.

THE CHLORIDES OF MERCURY.

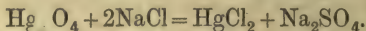
Mercurous Chloride Hg_2Cl_2 , often called *Calomel*, is formed as a white precipitate when the solution of any soluble Chloride, or Hydrochloric acid, is added to the solution of a Mercurous salt. On the large scale it is prepared by heating a mixture of Mercuric Chloride and Mercury :



It is almost insoluble in water ; 100 parts of water dissolve only .0002 part of Calomel. It is blackened by light, Mercury being set free. It is also turned black by contact with alkalis or Ammonia ; hence its name of Calomel, from the Greek word *kalomelas*, black.

It is used in small doses for medicine—blue pills contain this drug as a rule.

Mercuric Chloride HgCl_2 , also called *corrosive sublimate*, is made by heating a mixture of Mercuric Sulphate and Salt, when it sublimes in the form of white powder :



Mercuric Chloride is much more soluble in hot water than in cold, and can be obtained in rhombic crystals by cooling a hot saturated solution. This solution is a most valuable antiseptic, and is used for washing wounds and in surgical operations, though in a very dilute form—1 part HgCl_2 in 1000–2000 water.

Mercuric Chloride is a virulent poison. The antidote is Albumen or white of egg, which forms an insoluble compound with it.

Mercuric Iodide HgI_2 is obtained as a bright scarlet powder when Mercury and Iodine are rubbed together in a mortar in the presence of a little Alcohol.

When heated to 150°C ., this substance turns a bright yellow colour, but this yellow form is unstable at ordinary temperatures and becomes scarlet again if touched or rubbed.

When Mercury is treated with cold dilute Nitric acid, **Mercurous Nitrate**, $\text{Hg}_2(\text{NO}_3)_2$, is formed, but the hot strong acid gives **Mercuric Nitrate**, $\text{Hg}(\text{NO}_3)_2$. Both these Nitrates are soluble in water, but have a tendency to form basic salts, that is, salts containing the corresponding Oxide as well as the Nitrate, when boiled with a considerable quantity of water.

Detection of Mercury. All the salts of Mercury sublime when heated, and, if Sodium Carbonate is added to the salt before heating, the sublimate is formed as a mirror of Mercury on the sides of the tube.

Solutions of *Mercurous* salts give a white precipitate of Hg_2Cl_2 with Hydrochloric acid, which precipitate is blackened by the addition of Ammonia ; they also give a green precipitate of Hg_2I_2 with Potassium Iodide.

Solutions of *Mercuric* salts give a black precipitate of HgS with Sulphuretted Hydrogen, which is insoluble in Nitric acid ; they also give a scarlet precipitate of HgI_2 with Potassium Iodide.

When Stannous Chloride is added to a solution of a Mercuric salt in Hydrochloric acid, a white precipitate of Mercurous Chloride is first obtained by reduction, and as the operation proceeds further, a grey precipitate of metallic Mercury is formed.

PROBLEMS.

82. 5.26 grams of Mercuric Chloride are distilled with Lime, and the Mercury vapour evolved, when condensed, is found to weigh 3.88 grams. If the equivalent weight of Chlorine is 35.45, find that of Mercury.

83. .5 gram of an amalgam of Sodium and Mercury, when placed in water, evolved 38 c.c. of Hydrogen gas, measured over water at 10° C. and 765 mm. Find the percentage of Mercury in the amalgam.

CHAPTER XXXII.

THE ALUMINIUM GROUP OF ELEMENTS.

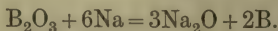
THIS group includes the two common elements Boron and Aluminium, with seven very scarce elements, three of which—Gallium, Indium and Thallium—are very closely related to Aluminium, but in the other four—Scandium, Yttrium, Lanthanum and Ytterbium—the relationship is not so marked. All the elements in the group are tri-valent, having Oxides with the general composition R_2O_3 and Chlorides RCl_3 . Boron exhibits no basic properties in its Oxide; the Oxide of Aluminium has both basic and acidic properties, whilst the Oxides of the rarer metals are uniformly basic in their properties.

BORON.

Symbol, B. Atomic Weight, 11.0.

Occurrence. The element Boron is always found combined in nature. As Boric acid, it is obtained from volcanic waters in Tuscany, and as Borates in the minerals *Tincal*, Sodium Borate, $Na_2B_4O_7 \cdot 10H_2O$, and *Boracite*, Calcium Borate, $Ca_2B_6O_{11}$.

Preparation. Boron is made by heating Boron Trioxide with either Sodium, Potassium or Aluminium in a covered crucible:



When the fused mass is treated with Hydrochloric acid, Boron separates out as a dark brown powder.

Properties. Boron is a dark brown powder, which is unacted upon by air. It is infusible even in the electric arc, but at high temperatures it combines with air, forming both Boron Trioxide, B_2O_3 and Boron Nitride, BN.

When boiled with oxidizing agents, such as Nitric or Sulphuric acids, it is converted into Boric acid, H_3BO_3 .

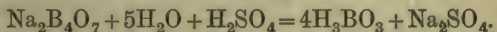
Boron may be dissolved in molten Aluminium, and on cooling crystals separate out, which were, at one time, thought to be an allotropic modification of Boron, but they are now considered to be a compound of Aluminium and Boron with a possible formula AlB_{12} .

COMPOUNDS OF BORON.

Boron exhibits tri-valency in all its compounds. It forms a Hydride BH_3 , compounds with the Halogens, viz. BF_3 , BCl_3 , BBr_3 and BI_3 , and an Oxide B_2O_3 . The last named can be made by heating Boron itself in air, or by heating Boric acid. It is a white powder, which unites readily with Water to form Boric acid.

Boric Acid, Boracic Acid, H_3BO_3 . The volcanic steam jets of the Tuscany marshes contain Boric acid, and the lagoons formed by the condensation of this steam are the source of considerable quantities of the acid, which is obtained from them by crystallizing concentrated solutions. The heat of the steam jets themselves is ingeniously used to concentrate the solutions.

Boric acid is also obtained by the action of dilute Sulphuric acid upon a hot concentrated solution of Borax; the acid crystallizes out when the solution is cooled :



Boric acid crystallizes in soft, white lustrous plates. It is not very soluble in cold water, but boiling water dissolves it well. It is more soluble in Alcohol than in water, and this solution burns with a characteristic green-tinged flame, and forms so delicate a method of detection that one milligram of Boric acid can be found by this means.

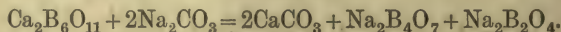
The aqueous solution is a weak acid ; it turns litmus a claret red, and yellow turmeric paper is coloured brown by it. Like Carbonic acid, Boric acid does not affect Methyl Orange. Phenolphthalein may be used as an indicator in titrations of Boric acid with Caustic Soda, but a little Glycerin must be added to prevent Hydrolysis, or the indicator will change colour before the reaction is complete.

Boric—or as it is often called, Boracic—acid is extensively used as an antiseptic, in the form of washes, as Boric lint and Boric ointment.

Boric acid, like Phosphoric acid, forms three series of salts derived from (1) Orthoboric acid, H_3BO_3 , (2) Metaboric acid, HBO_2 and (3) Pyroboric or Biboric acid, $\text{H}_2\text{B}_4\text{O}_7$.

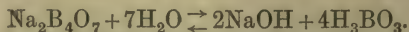
Of these the Orthoborates and Metaborates are of little interest or importance, and only the Biborates are worth considering in this place. By far the most important of these is Sodium Biborate or Borax, $\text{Na}_2\text{B}_4\text{O}_7$ or $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$.

Borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ occurs as the mineral *Tincal* in Thibet, Northern India and California, where it has been deposited by the drying up of inland lakes. Large deposits of *Boracite*, Calcium Borate, occur in Bolivia, and Borax is obtained from this mineral by boiling it with a solution of Sodium Carbonate :



Chalk is precipitated, and the solution contains Borax and Sodium Metaborate. The latter is converted into Borax by blowing Carbon Dioxide through its solution.

Borax is only sparingly soluble in cold water—1.6 grams in 100 grams of water at 0° —but 100 grams of boiling water dissolve 52.5 grams of the salt. This solution is alkaline, owing to hydrolysis, Boric acid being a “weak” acid and not ionizing freely :



When crystalline Borax is heated, it swells up, loses Water and finally melts to a clear glass, which is anhydrous Borax. Fused Borax dissolves many of the metallic Oxides, which give

to the glass characteristic colours. The Borax "heads" used in analysis are based on this fact.

COLOURS OF BORAX BEADS.

Metallic Oxide.	Oxidizing Flame.	Reducing Flame.
Copper - - -	Green (hot), blue (cold).	Red or colourless.
Cobalt - - -	Blue.	Blue.
Iron - - -	Brown (hot), yellow (cold).	Olive green.
Nickel - - -	Violet (hot), yellowish brown (cold).	Grey and opaque.
Manganese - -	Amethyst.	Grey and opaque.

Borax is used, in large quantities, in the manufacture of enamels, glazes and glass. It is also a mild antiseptic, and is used for preserving food of various kinds. It is useful as a flux and for soldering and brazing, as it dissolves the metallic Oxides and renders the surface of the metal clean.

ALUMINIUM.

Symbol, Al. Atomic Weight, 27.1.

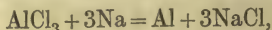
Occurrence. Aluminium, in combined form, is one of the most widely distributed elements in the earth's crust; it is the third most abundant element—Oxygen and Silicon being first and second respectively.

As Aluminium Oxide, Al_2O_3 , it is found in *Sapphire*, *Ruby* and *Corundum*. *Emery* is Corundum with a little Iron Oxide. *Bauxite* is the name given to various minerals, which are Hydroxides of Aluminium, and from which the metal itself is principally obtained.

Cryolite is a double Fluoride of Aluminium and Sodium $\text{Al}_2\text{F}_6 \cdot 6\text{NaF}$, and *Turquoise* is a hydrated Phosphate of Aluminium. Besides these minerals, Aluminium is most widely distributed in the form of Silicate; *Clay* consists

largely of this compound, and all the *Felspars* contain it to a greater or less degree.

Preparation. Aluminium was first isolated by Wohler in 1845 by heating Aluminium Chloride with Sodium :



and for a long time it was considered a chemical curiosity. Its price in 1855 was £120 per kilo, the present price per kilo is about 1s. 3d. This reduction has been brought about by the use of an electrolytic process for the separation of the metal.

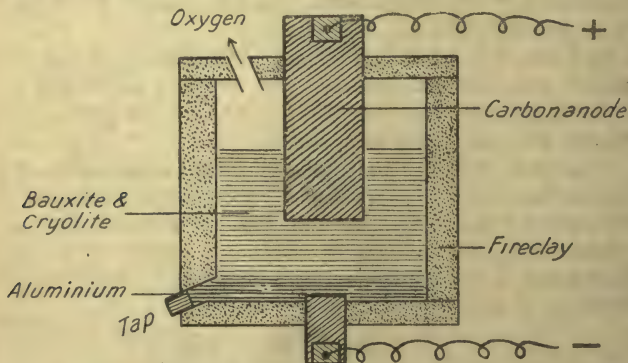


FIG. 150.—Electrolytic manufacture of Aluminium. (Diagrammatic.)

A solution of Bauxite in fused Cryolite was found to be an electrolyte, and this is used in an "electrolytic cell," a diagrammatic form of which is shewn in Fig. 150. The operation is conducted in a fireclay receptacle, a Copper cathode and a Carbon anode being used. A mixture of Cryolite and Bauxite with a little Aluminium is used to start with. This is melted by the electric arc, the poles being, at first, close together; the molten Aluminium then forms the cathode, the Carbon anode is raised and electrolysis proceeds. Fresh charges of Bauxite are introduced through the aperture at the top, through which also the Oxygen produced by the electrolysis escapes. Molten Aluminium is drawn off, from time to time, by the tap.

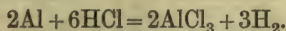
Properties. Aluminium is a bluish-white metal, which is capable of taking a high polish. It is very strong, and as it is also very light (density 2.6), it is very useful for articles in which both strength and lightness are required. Added to this, it does not tarnish in dry or moist air, though at fairly high temperatures a superficial layer of Oxide is formed on its surface, which seems to protect the rest of the metal. Thin Aluminium foil burns in Oxygen at a high temperature, emitting a brilliant white light.

Aluminium is a very electro-positive element, and its powder unites readily with Oxygen at a high temperature, and is therefore a strong reducing agent.

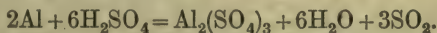
Mixtures of powdered Aluminium with various Oxides ignite readily when heated and give out tremendous heat; such mixtures are sold under the name of *Thermite*, and are used for welding Iron and other purposes.

A mixture of Iron Pyrites and powdered Aluminium ignites at once when heated, producing a temperature of over 3000° C.; Aluminium Sulphide and metallic Iron are left behind.

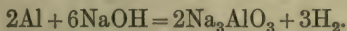
Nitric acid, either strong or dilute, has very little action on Aluminium, but Hydrochloric acid dissolves it readily with the evolution of Hydrogen:



Hot concentrated Sulphuric acid also dissolves it with the evolution of Sulphur Dioxide:



Caustic Alkalies readily dissolve Aluminium, Hydrogen being evolved and the Aluminate of the metal left behind:



Alloys. The most important alloy of Aluminium is *Aluminium Bronze*, which contains 90 per cent. of Copper and 10 per cent. of Aluminium. This alloy has the colour of Gold, and is not tarnished by air at all. It is quite as strong as steel, and as it is also malleable and gives good castings, it is a most valuable alloy, and is used for many purposes. *Magnalium*

contains 90 per cent. of Aluminium with Magnesium and other metals, and as it is more readily turned than Aluminium and is stronger, it is often employed instead of the pure metal.

Uses. Aluminium paint is a mixture of oil and powdered Aluminium, and forms a covering unaffected by air or moisture. The metal is also used for cooking utensils, military outfits, balances, parts of airships, etc., etc.; in fact, everything where strength and lightness are required.

Aluminium wire is used for electrical purposes, for though it is not so good a conductor as Copper, it is much lighter and does not strain the supports; hence it is often used in aërials for wireless telegraphy. It has one defect—it is very difficult to make a good join in Aluminium wire by soldering.

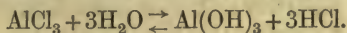
COMPOUNDS OF ALUMINIUM.

Aluminium Oxide, Alumina, Al_2O_3 . This compound, as has already been stated, occurs native in many forms. When pure and colourless it forms *Corundum*, and, when tinted with minute quantities of metallic Oxides, it forms *Ruby*, *Sapphire* and *Amethyst*. These gems can all be made artificially by melting Alumina in an electric furnace with proper quantities of the different metallic Oxides—Chromium, Cobalt and Manganese.

Aluminium Hydroxide $\text{Al}(\text{OH})_3$ is obtained as a gelatinous precipitate when Ammonia or a Caustic Alkali is added to the solution of an Aluminium salt. The precipitate dissolves even in slight excess of the reagent, but the presence of Ammonium Chloride ensures the precipitation. This precipitate is readily soluble in acids, forming the salts of Aluminium.

When a precipitate of Aluminium Hydroxide is formed in the presence of colouring matter, the latter is precipitated with it, forming what is technically known as a “lake.” This fact is made use of in the process of dyeing. The Hydroxide is precipitated in the fibres of the cloth, this is then dipped in the dye, which is “fixed” in the Aluminium Hydroxide. The latter substance and other substances which behave in a similar way are known as *mordants*:

Aluminium Hydroxide behaves as if it were both a basic and an acidic Oxide, but it is both a "weak" base and a "weak" acid. As a basic Oxide, it dissolves in acids, forming Aluminium salts, but the solutions of all these salts are acid to litmus, owing to hydrolysis, the Hydroxide being a "weak" base and not ionizing freely. Thus, for Aluminium Chloride,



Free Hydron is present in the solution, owing to the "strong" Hydrochloric acid and "weak" Aluminium Hydroxide.

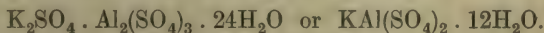
The acidic properties of Aluminium Hydroxide are seen in its solution by alkalies with the formation of salts called *Aluminates*. Sodium Aluminate is a representative of these salts, and may be reckoned as a compound of Sodium Oxide and Alumina, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$, though its formula is usually written NaAlO_2 . Solutions of these salts in water hydrolyse freely, and are alkaline to litmus, owing to the feeble acidity of Aluminic acid.

The Aluminates are found as minerals, examples being *Spinel*, Magnesium Aluminate, $\text{MgO} \cdot \text{Al}_2\text{O}_3$; *Chrysoberyl*, Beryllium Aluminate, $\text{BeO} \cdot \text{Al}_2\text{O}_3$; and *Gahnite*, Zinc Aluminate, $\text{ZnO} \cdot \text{Al}_2\text{O}_3$.

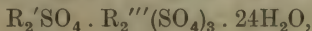
Aluminium Sulphate $\text{Al}_2(\text{SO}_4)_3$ can be made by dissolving Aluminium Hydroxide in Sulphuric acid.

It is made on a large scale by dissolving Bauxite and the purer kinds of clay in Sulphuric acid, and as so prepared is called "Alum cake." Its solution in water has an acid reaction, and will evolve Hydrogen when Zinc is placed in it.

The Alums. Aluminium Sulphate forms a remarkable series of double salts with the Sulphates of mono-valent metals. If hot solutions of the Sulphates of Aluminium and Potassium are mixed together and allowed to cool, colourless octohedral crystals are deposited, which have a formula



These are known as *Potash Alum* or simply *Alum*. It is the chief representative of a series of isomorphous double Sulphates called the Alums, which have a general formula :



where R' represents a mono-valent metal or radicle, Sodium, Potassium, Ammonium, Rubidium, Caesium or Silver, and R''' represents a tri-valent metal, Aluminium, Iron, Chromium or Manganese.

Ordinary Alum is very much more soluble in hot water than in cold. At 0°C ., 100 parts of water dissolve only 3.9 parts of Alum, but at 100°C . they will dissolve 357 parts of the salt.

When heated Alum begins to part with its water of crystallization at 42°C ., and, at a dull-red heat, all the water is driven off, and the white powder remaining is called *burnt alum*.

The chief use of Alum is as a mordant in dyeing; its action has been described above. It is also used for waterproofing cloth fabrics by the precipitation of Aluminium Hydroxide in the fibres of the cloth.

Clays. Many of the mineral constituents of igneous rocks—notably the Felspars—contain a large percentage of Aluminium Silicate. When such an igneous rock—Granite, for example—is subjected to the influence of atmospheric agencies, *e.g.* heat, frost, percolating water containing Carbon Dioxide, or vegetable acid, etc., it begins to disintegrate; the process is called “weathering” by geologists. In the process of disintegration, the Felspar, which is the principal constituent of Granite, is attacked first, especially if the water contains an alkaline Carbonate, and breaks down, leaving a white insoluble Aluminium Silicate. This is washed away from the insoluble Quartz and Mica in the Granite, and forms very pure white deposits, which are called *China Clay* or *Kaolin*. These deposits are formed *in situ*, but if the clay is washed away by streams, other minerals, most often of a ferruginous nature, become mixed with the Aluminium Silicate, and, when deposited, the clay is coloured and impure.

Clays of all kinds possess the most useful property of being plastic enough to be moulded into any shape when they are wet and of retaining that shape when strongly heated, forming a hard coherent mass. They are used in the manufacture of articles too numerous to mention.

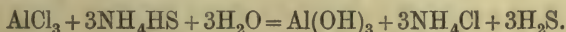
After being “fired,” the result is called “biscuit,” and is

quite porous. For most purposes it is next covered with a "glaze" by dipping it into a mixture of Lead Silicate, Clay, Felspar, etc., suspended in water, and "firing" a second time. The result is called *earthenware*, and it may be decorated, either by painting designs on the biscuit before glazing or by painting fusible enamels on the glaze itself. The cheap red earthenware crocks are glazed by introducing Salt into the furnace; this covers the article with a brown glass-like skin.

In the making of "porcelain," a certain quantity of Quartz and Felspar is mixed with the China clay before moulding, and this gives, on firing, a glass-like quality to the resultant article which does away with the necessity of glazing.

Detection of Aluminium. Compounds of Aluminium, when heated on Charcoal, give a white infusible residue of Alumina, which, with a few drops of Cobalt Nitrate, yields a bright blue mass on reheating.

Solutions of Aluminium salts give white gelatinous precipitates of $\text{Al}(\text{OH})_3$ with either Ammonia or a Caustic alkali; these precipitates are soluble in excess of the reagent. A similar gelatinous precipitate of Aluminium Hydroxide is obtained when Ammonium Sulphide is added to the solution of a salt of Aluminium:



PROBLEMS.

84. .573 gram of crystalline Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$) left on heating .303 gram of the anhydrous Salt. Find x .

85. 100 parts of Aluminium Sulphate ($\text{Al}_2(\text{SO}_4)_3$) gave 29.934 parts of Alumina (Al_2O_3). Given $\text{S}=32$ and $\text{O}=16$, calculate the Atomic Weight of Aluminium.
(Camb. Univ. Schol. Exam.)

PRACTICAL EXERCISES.

To prepare crystals of Boric acid from Borax. Make a hot concentrated solution of Borax in distilled water. Add about 25 c.c. of dilute Sulphuric acid and allow the liquid to cool. The crystals which separate out are those of Boric

acid. Pour off the liquid above the crystals, wash with a few c.c. of distilled water and filter. Dry the crystals on the filter paper.

To test the crystals for Boric acid, dissolve a little in a small quantity of distilled water, add about 10 c.c. of Methylated Spirits and set fire to the Spirit ; if Boric acid is present, the flame will be tinged green by it.

CHAPTER XXXIII.

THE METALS OF THE CHROMIUM GROUP.

CHROMIUM is by far the most important member of a group of elements, of which the other members are Molybdenum, Tungsten and Uranium. The metals of the group are characterized by their infusibility, and by the fact that they all unite with Oxygen, Sulphur, Nitrogen and the Halogens when heated in these gases. They all form acidic Trioxides, CrO_3 , MoO_3 , WO_3 and UO_3 , from which a series of isomorphous salts with the general formula K_2RO_4 are obtained. These salts are also isomorphous with the Sulphates, by which the relationship between these elements and Sulphur is established. Molybdenum and Uranium are characterized by the large number of different Oxides—each element has five at least—which have been isolated.

Chromium also possesses affinities with tri-valent Ferric Iron, and with Aluminium and Manganese, which can be investigated by the student.

CHROMIUM.

Symbol, Cr. Atomic Weight, 52.0.

Occurrence. The principal ore of Chromium is the mineral *Chrome Iron ore* or *Chromite*, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, which is one of the members of the isomorphous Spinel group of minerals.

Preparation. Chromium is prepared from its Sesquioxide, Cr_2O_3 by the *Aluminothermic* process. A mixture of this Oxide and Aluminium powder is placed in a refractory clay

crucible till it is two-thirds full, the crucible being placed in a tray of sand (Fig. 151). The mixture has a heap of a mixture

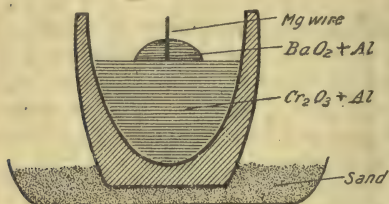
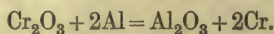


FIG. 151.—Aluminothermic process for making Chromium.

of Barium Peroxide and Aluminium powder on its surface, in which is placed a short length of Magnesium wire. This latter is set alight and starts the combustion, intense heat is developed and the reduction of the Chromium Oxide is brought about by the

Aluminium, a button of metallic Chromium being found at the bottom of the crucible when the action is finished :



Properties. Chromium is a steel-grey metal which melts at 1500°C . It does not change in air at ordinary temperatures, but oxidizes when heated.

It dissolves in Hydrochloric and Sulphuric acids with the evolution of Hydrogen, but in strong Nitric acid it becomes inert or "passive" like Iron (p. 469).

It is used for alloying with Steel, an alloy containing 3 or 4 per cent. of Chromium is so hard that a Steel drill will not touch it. This alloy can, however, be welded to Iron, and is used for a variety of purposes where extreme toughness is required, such as for burglar-proof safes, for stamping mills and for the armour-plating of men-of-war.

COMPOUNDS OF CHROMIUM.

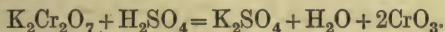
Chromium forms two compounds with Oxygen, the Sesquioxide, Cr_2O_3 , which is basic and from which the Chromic salts may be obtained, and the Trioxide, CrO_3 , which is acidic and forms the important series of salts—the Chromates and the Bichromates.

Chromium Sesquioxide Cr_2O_3 is a green powder obtained

by heating the Hydroxide, $\text{Cr}_2(\text{OH})_6$, or the Trioxide, CrO_3 . It is used as a pigment and for imparting a green colour to glass.

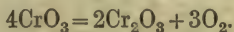
Chromic Sulphate $\text{Cr}_2(\text{SO}_4)_3$ can be obtained in violet blue crystals from a solution of the Hydroxide in Sulphuric acid. With Potassium Sulphate, it forms a double salt—the well-known *Chrome Alum*, $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$. This substance crystallizes in dark plum-coloured octohedra, which are often found deposited from the solution of a Bichromate battery when it is run down.

Chromium Trioxide CrO_3 is formed, as scarlet needle-shaped crystals, when a strong solution of Potassium Bichromate is acted upon by concentrated Sulphuric acid, and the solution is cooled :



The crystals of Chromium Trioxide are very deliquescent and form a red acid solution with water. The acid is most probably Dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$, as H_2CrO_4 has not been isolated.

When heated to 250°C . Chromium Trioxide decomposes into Chromium Oxide, Cr_2O_3 and Oxygen. It may therefore be looked upon both as a Peroxide and an acidic Oxide :



On account of the readiness with which it gives up part of its Oxygen, it is a powerful oxidizing agent. It chars paper, and so a strong solution cannot be filtered, and warm Alcohol takes fire when dropped on crystals of the Trioxide.

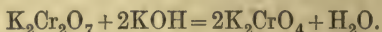
This power of oxidation is transmitted to its salts the Chromates and Bichromates, these compounds being extremely useful oxidizing agents.

CHROMATES AND BICHROMATES.

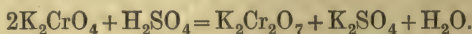
Chromium Trioxide forms two important series of salts with basic Oxides. In the Chromates one molecule of the Trioxide is united with one molecule of the basic Oxide,

e.g. Lead Chromate, PbCrO_4 , *i.e.* $\text{PbO} \cdot \text{CrO}_3$, and Potassium Chromate, K_2CrO_4 , *i.e.* $\text{K}_2\text{O} \cdot \text{CrO}_3$, whilst in the Bichromates there are two molecules of the Trioxide united to one molecule of the basic Oxide, *e.g.* Potassium Bichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, *i.e.* $\text{K}_2\text{O} \cdot 2\text{CrO}_3$.

Chromates are formed from Bichromates by the addition of an Alkali, thus :



Bichromates are formed from Chromates by the addition of an acid, thus :



Potassium Chromate K_2CrO_4 may be prepared from the Bichromate by the reaction stated above. It forms bright yellow rhombic crystals, which are isomorphous with those of Potassium Sulphate, K_2SO_4 .

It is used as a reagent in the laboratory, as most of the metallic Chromates, *e.g.* Lead, Silver, Mercury, Barium, etc., are insoluble in water and are precipitated when a solution of Potassium Chromate is added to a solution of a soluble salt of the metal.

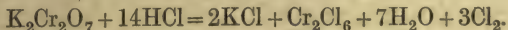
It is also an oxidizing agent, but is not so powerful or so much used in this respect as Potassium Bichromate.

Potassium Bichromate $\text{K}_2\text{Cr}_2\text{O}_7$ is made in considerable quantities from Chrome Iron ore. The ore is fused with a mixture of Potassium Nitrate and Carbonate, and the fused mass is extracted with water. The solution contains Potassium Chromate, and this is treated with Sulphuric acid, and, on concentration and cooling, the sparingly soluble crystals of the Bichromate separate out.

Potassium Bichromate forms bright red crystals which dissolve in water, forming an alkaline solution, owing to the fact that Chromic acid is a "weak" acid.

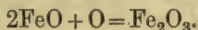
It is used largely for Bichromate batteries and other purposes, and also as an oxidizing agent. Its reduction is accompanied by the change of colour of its solution from red to green, owing to the formation of Chromic salts.

When Potassium Bichromate is acted upon by Hydrochloric acid, the latter is oxidized and Chlorine gas is evolved :

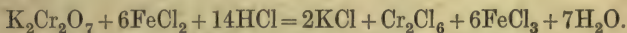


The oxidizing power of Potassium Bichromate depends upon the fact that the two molecules of CrO_3 contained in the molecule $\text{K}_2\text{Cr}_2\text{O}_7$ break down, forming one molecule of Cr_2O_3 , so that three atoms of Oxygen are set free for Oxidizing purposes.

It is used in the oxidation of Ferrous compounds to Ferric compounds. Now two molecules of Ferrous Oxide require one atom of Oxygen to form one molecule of Ferric Oxide, thus :



Therefore, the three spare Oxygen atoms in one molecule of $\text{K}_2\text{Cr}_2\text{O}_7$ are capable of turning six molecules of Ferrous Oxide (or any Ferrous salt) into Ferric Oxide (or the corresponding Ferric salt), *e.g.* :



It is used in this way in the volumetric estimation of Iron (p. 476).

Detection of Chromium. Chromium salts impart a green colour to the Borax bead in both the oxidizing and reducing flames.

When heated on Platinum foil with fusion mixture (Potassium Nitrate and Sodium Carbonate), a yellow mass containing Potassium Chromate is formed, which, when dissolved in water, gives a yellow precipitate of Lead Chromate with Lead Acetate solution.

Soluble salts of Chromium give a green precipitate of $\text{Cr}_2(\text{OH})_6$ when either Ammonia, Ammonium Sulphide or Caustic Soda is added to the solution.

PROBLEM.

86. .2291 gram of Ammonium Bichromate $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ gave, on ignition, .1382 gram of Chromium Sesquioxide Cr_2O_3 . Calculate the Atomic Weight of Chromium from these data, given those of Hydrogen, Oxygen and Nitrogen.

PRACTICAL EXERCISES.

To prepare metallic Chromium from Chromium Oxide. The method to be employed is the Aluminothermic process described on page 450 (Fig. 151).

To prepare crystals of Chromium Trioxide. Take about 50 c.c. of a saturated solution of Potassium Bichromate in a beaker. Add gradually 25 c.c. of strong Sulphuric acid. When the liquid cools, crystals of Chromium Trioxide separate out. Pour off the acid liquid from above the crystals, wash with a little distilled water and pour off the water from the crystals. Dry the crystals on a watch-glass in a steam oven, *not* on filter paper.

Prove by the tests given on page 33 that Chromium Trioxide is both acidic and a peroxide.

CHAPTER XXXIV.

MANGANESE AND ITS COMPOUNDS.

MANGANESE.

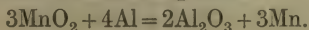
Symbol, Mn. Atomic Weight, 54.9.

THE element Manganese is found in the same group as the Halogens in the Periodic classification of the elements, but its resemblance lies in the fact that its Heptoxide, Mn_2O_7 , resembles the similar Chlorine Oxide, Cl_2O_7 , and the salts derived from these Oxides—the Permanganates, $\text{R}'\text{MnO}_4$, and the Perchlorates, $\text{R}'\text{ClO}_4$,—are isomorphous. In all its other compounds and in its general properties, Manganese differs widely from all the members of the Halogen groups, and is very much more allied to the metals Chromium and Iron.

For example, the metals themselves resemble one another in physical and chemical properties; they all possess Sesquioxides with the general formula R_2O_3 , and the Sulphates formed from these Sesquioxides form isomorphous Alums, *e.g.* Chrome, Manganese and Iron Alums.

Occurrence. Manganese is found, principally, united with Oxygen, the chief minerals being *Pyrolusite*, MnO_2 , which is by far the most common Manganese mineral, *Braunite*, Mn_2O_3 and *Manganite*, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Traces of Manganese compounds provide the colouring agent in most of the amethyst-coloured gems and minerals.

Preparation. Manganese is best prepared in a similar manner to Chromium (p. 450) by igniting a mixture of Manganese Dioxide and Aluminium powder :



Properties. Manganese is a grey metal with a slight tinge of red in it. It is very hard and brittle. It melts at 1245°C .

It is slightly oxidized in moist air, and slowly decomposes Water with the evolution of Hydrogen. It is quite easily dissolved by dilute acids—Hydrochloric, Sulphuric and Acetic—giving off Hydrogen and forming Manganous salts.

Manganese metal is used for various alloys, such as *Manganese Bronze*, *Ferro-manganese* and *Manganese Steel*. The last-named is a particularly hard metal, and is used for milling plates and for the armour-plating of ships.

COMPOUNDS OF MANGANESE.

Manganese forms more Oxides than any other element. No less than six are known: MnO , which is Basic; Mn_3O_4 , like Fe_3O_4 ; Mn_2O_3 , which is Basic; MnO_2 , which is both Basic, a Peroxide and Acidic; MnO_3 , which is Acidic; and Mn_2O_7 , which is also Acidic.

It has probably been noticed by the student that when an element forms several Oxides, the higher ones are Acidic and the lower ones more Basic.

Manganese forms two series of salts—the Manganous salts derived from Manganous Oxide, MnO , in which the element is di-valent, and the Manganic salts derived from Manganic Oxide, Mn_2O_3 , in which Manganese exhibits tri-valency.

Manganese Dioxide MnO_2 is the most important Oxide of Manganese, and is found, in some quantity, as the mineral *Pyrolusite*. It is largely used in the manufacture of Chlorine gas, as the oxidizing agent in Leclanché batteries, and for the making of Permanganates, such as Condy's fluid.

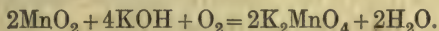
Manganese Dioxide acts as a Peroxide when heated, evolving Oxygen and leaving behind Trimanganic Tetroxide:



It acts, with alkalis, as a feeble Acidic Oxide, forming salts called Manganites.

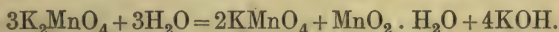
THE MANGANATES AND PERMANGANATES.

When Manganese Dioxide is strongly heated with Caustic Potash, and an oxidizing agent such as Saltpetre or Potassium Chlorate, a dark green mass is obtained, which contains Potassium Manganate, K_2MnO_4 :



This mass dissolves in water, forming a green solution, from which, by careful evaporation in vacuo, dark green crystals of the Potassium Manganate, K_2MnO_4 , can be obtained. These crystals are isomorphous with the corresponding Sulphates and Chromates, and form another point of resemblance between Manganese and Chromium.

If the dark green solution of Potassium Manganate is warmed or diluted with a large quantity of water, its colour changes to a bright pink, owing to the formation of Potassium Permanganate, $KMnO_4$, and at the same time a precipitate of hydrated Manganese Dioxide is thrown down, thus :



When the solution is concentrated, it forms dark purple crystals, which are isomorphous with those of Potassium Perchlorate, $KClO_4$.

The solution of Potassium Permanganate is of a deep purple colour, if at all strong ; very dilute solutions have a rose-pink colour. When the solution is acidified, there is no change in its appearance, but the liquid now contains Permanganic acid, $HMnO_4$.

Potassium Permanganate, when heated to a temperature of $250^\circ C.$, breaks up, forming Potassium Manganate, Manganese Dioxide and Oxygen :



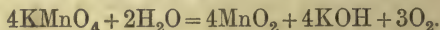
The readiness with which Potassium Permanganate parts with its Oxygen makes it a valuable oxidizing agent.

There are three stages in the reduction of the Permanganate :

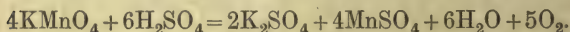
- (1) By boiling with an alkali, Potassium Manganate is first formed, thus :



- (2) If a mild reducing agent is present in the solution, further reduction to Manganese Dioxide takes place :

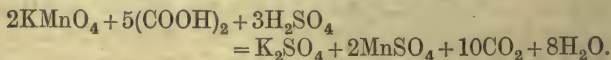


- (3) In acid solutions, still more reduction takes place, and a Manganous salt is formed :

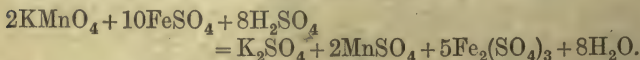


This reduction in acid solutions is brought about by many substances, *e.g.* Oxalic acid, Ferrous Sulphate, Hydrogen Peroxide, etc., and the reaction is made use of, in volumetric analysis, for the quantitative determination of these substances.

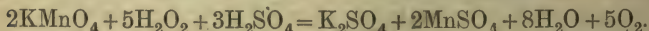
With Oxalic acid the reaction is represented thus :



With Ferrous Sulphate action takes place as follows :



With Hydrogen Peroxide there is the interesting action of two oxidizing agents mutually reducing one another :



On account of their strong oxidizing properties, Permanganates are valuable as disinfectants, and the solution of crude Sodium Permanganate in water forms the well-known *Condy's Fluid*.

Detection of Manganese. Manganese compounds give an amethyst tinge to a Borax bead in the oxidizing flame, but the bead is colourless in the reducing flame.

When heated on Platinum foil with Sodium Carbonate and Saltpetre, they give a green mass containing the Manganates.

Solutions of Manganese salts yield a flesh-coloured precipitate of MnS with Ammonium Sulphide, and a white precipitate of $Mn(OH)_2$ with Caustic Soda.

PROBLEMS.

87. Determine the weight of Manganese Dioxide, which, when acted upon by Hydrochloric acid, will yield sufficient Chlorine to combine exactly with the Hydrogen evolved when 5 grams of Zinc are acted upon by dilute Sulphuric acid.

88. What weight of Potassium Permanganate is required to completely decompose 20 c.c. of a "20 volume" solution of Hydrogen Peroxide at 0° and 760 mm. ?

PRACTICAL EXERCISES.

To prepare crystals of Potassium Permanganate. Grind up in a mortar a mixture of (roughly) 1 part of Manganese Dioxide, 2 parts of Saltpetre and 2 parts of Caustic Potash. Place some of the mixture in a porcelain crucible (a Platinum crucible is better if available), and heat strongly by means of a foot blowpipe or in a muffle furnace for ten minutes.

Digest the contents of the crucible with warm water. The green solution formed contains Potassium Manganate, and will change, if heated for a short time, into a deep mauve solution of Potassium Permanganate.

Pour the liquid away from the deposited Manganese Dioxide while still hot and allow it to cool. Crystals of Potassium Permanganate should form, if not, the liquid must be concentrated by boiling and cooled again.

To determine the percentage of Manganese Dioxide in a specimen of Pyrolusite. Weigh out 1 gram of the Pyrolusite, place it in a flask (Fig. 152), and add about 25 c.c. of pure strong Hydrochloric acid. Connect the flask with two U-tubes joined together as in the diagram, each containing a solution of Potassium Iodide and being kept cool by immersion in water. Boil the contents of the flask till all the Chlorine has been driven off. This Chlorine will liberate an equivalent quantity of Iodine from the Potassium Iodide.

When the action has ceased, wash the contents of the two U-tubes into a large flask and determine the weight of Iodine present by means of Sodium Thiosulphate solution (p. 241).

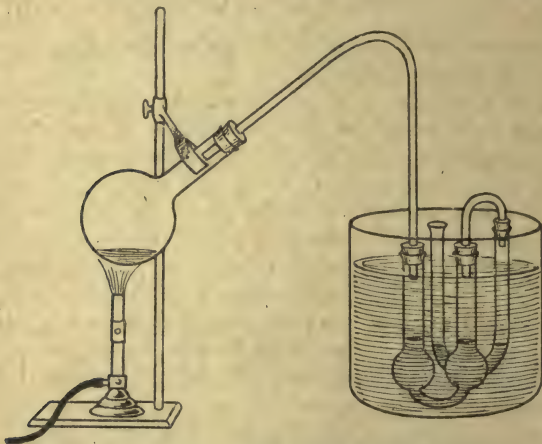
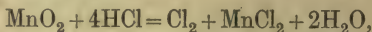


FIG. 152.—Percentage of Manganese Dioxide in Pyrolusite.

Now 127 grams of Iodine are equivalent to 35.5 grams of Chlorine; hence the weight of Chlorine which was evolved can be ascertained.

From the equation,

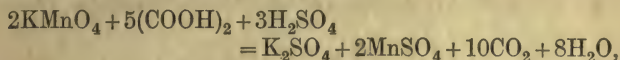


it is evident that 71 grams of Chlorine gas are liberated by using 87 grams of Manganese Dioxide. Hence the percentage of Manganese Dioxide in the Pyrolusite can be found.

To study the effect of Potassium Permanganate on Oxalic acid. Make a solution of Oxalic acid, add a few c.c. of Sulphuric acid, *warm the mixture* and then add Potassium Permanganate solution gradually. At first the Permanganate solution is decolourized, but when all the Oxalic acid is fully oxidized, the solution remains pink.

This reaction may be used for determining, by volumetric

analysis, the quantity of Oxalic acid (or of an Oxalate) present in any solution. From the equation,

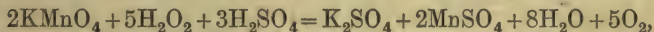


it is seen that 316 grams of Potassium Permanganate will Oxidize 450 grams of Oxalic acid.

Make up a standard solution of Potassium Permanganate by dissolving 3.16 grams of pure crystals in a litre of water. Every c.c. of this solution is equivalent to .0045 gram of Oxalic acid.

In performing the titrations, place the Permanganate solution in the burette, add a little Sulphuric acid to the Oxalic acid (or the Oxalate) before titrating, and *keep the liquid hot* during titration. The Permanganate acts as its own indicator, the least excess producing a pink tinge in the liquid.

The same solution of Potassium Permanganate may be used to find the strength of a solution of Hydrogen Peroxide. From the equation,



it is seen that 316 grams of Potassium Permanganate react with 170 grams of Hydrogen Peroxide. Hence 1 c.c. of the Permanganate solution prepared as described above is equivalent to .0017 gram of Hydrogen Peroxide.

In performing this titration, some dilute Sulphuric acid must be added first, and the liquid must be kept cool.

CHAPTER XXXV.

IRON, COBALT AND NICKEL.

THE three metals Iron, Cobalt and Nickel form one of the three isolated groups of what are called Transition elements in the Periodic series of the classification of the elements. Their Atomic Weights are very nearly equal to one another, and also to that of Manganese, which element is allied to them in some of its properties and its compounds.

The three metals Iron, Cobalt and Nickel are very alike in appearance; they all possess magnetic properties, which, however, are comparatively feeble in Nickel and Cobalt. Their behaviour towards acids is very similar, but, on the other hand, Iron rusts in moist air and the other two metals do not.

All three elements exhibit both di-valency and tri-valency in their Oxides, and all possess Oxides with the general formulae RO , R_2O_3 and R_3O_4 . In their salts Iron and Cobalt exhibit both di-valency and tri-valency, but, so far, no tri-valent salts of Nickel have been prepared.

IRON.

Symbol, Fe (Ferrum). Atomic Weight, 55.85.

History. Iron is, by far, the most useful to man of all the metals, and was one of the earliest to be made use of. Iron implements were found in a pyramid at Gizeh in Egypt,

dating from B.C. 3000. Amongst the old alchemists Iron was associated with Mars, the god of war, probably from the use of weapons made of this metal.

Occurrence. Iron is found native in small particles disseminated through masses of basaltic rocks, and also in meteorites, which vary in size from fine impalpable powder observed in the Arctic snows to huge masses many tons in weight. Its principal compound in nature is Ferric Oxide Fe_2O_3 . This is found in the pure state as *Haematite*, and associated with varying quantities of water in *Brown Haematite*, $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, in *Limonite*, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, in *Göthite*, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and in *bog iron ore*, whose composition is very variable. A very pure ore of Iron is *Magnetite* Fe_3O_4 , which is also called the *loadstone* from its magnetic properties. *Siderite* or *Chalybite*, Ferrous Carbonate, FeCO_3 , and *Iron Pyrites*, FeS_2 are other ores of Iron which occur in some quantity.

Preparation. The reduction of Ferric Oxide to metallic Iron is not a matter of any great difficulty, and, in practice, is usually brought about by the aid of Coke. When pure *Haematite* is the ore used, the method is simple, but complications are brought about by the presence of impurities. The ore is first *calcined* in a kiln, where a mixture of ore and Coal is fed into the top, takes fire in the lower part of the kiln, and calcined ore is taken out from the bottom. By this process Water and Carbon Dioxide are driven off, and most of the Sulphur present is oxidized to Sulphur Dioxide and escapes.

The calcined ore, which is now more porous than before, is mixed with Coke and Limestone and smelted in a blast furnace (Fig. 153). Such a furnace is usually from 70–80 ft. high, and about 20 ft. wide in its widest part. The mixture of calcined ore, Coke and Limestone is “fed” in from the gallery round the top of the furnace by means of a cup and cone feeder. The temperature in the furnace ranges from 500°C . at the top to over 1100°C . at the base, where the combustion of the Coke takes place, and is aided by strong blasts of hot air led into the furnace by *twyers* (from the

French *tuyères*). The process is a continuous one, furnaces often being kept going for years without "blowing out," and the chemical actions which take place in the furnace are somewhat as follows:

Near the hot blast, the Coke is burnt to Carbon Dioxide, which is probably at once reduced to Carbon Monoxide by the red-hot Carbon. The Limestone splits up into Lime and

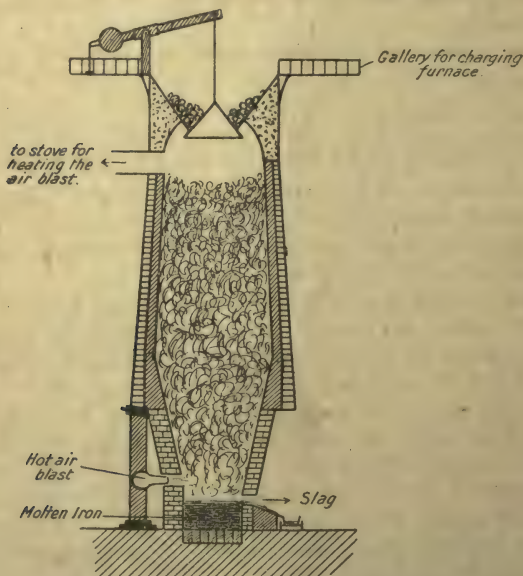
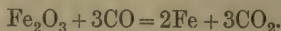


FIG. 153.—Diagrammatic section of a Blast Furnace.

Carbon Dioxide, which latter is also to some extent reduced by the hot Carbon to the Monoxide. The ascending Carbon Monoxide meets the Ferric Oxide in the ore, and reduces it to spongy metallic Iron:



The Iron melts when it reaches the base of the furnace and forms a liquid layer of molten metal, which is "tapped" off from time to time and run into moulds of sand, where it solidifies, forming *pig iron*. Meanwhile the Lime, formed by the reduction of the Limestone, unites with the Silica (sand) and some of the other impurities in the ore, and forms a fusible *slag*, which floats on the surface of the molten Iron. It is drawn from the furnace into trucks and taken to the slag heap, where it solidifies, and is afterwards used for road metal or railway ballast.

The composition of the gases which escape at the top of the furnace is roughly :

CO.	CO ₂ .	N.	H.	Hydrocarbons.
25.3	10.5	58.1	4.3	1.6 per cent.

It is thus seen to be a combustible mixture, and by burning it in a suitable stove, the heat evolved is used for heating the air for the hot-air blast, for calcining the ore and for heating engine boilers.

Pig Iron or Cast Iron is by no means a pure form of the metal. It usually contains from 2 to 4½ per cent. of Carbon, which is present, as a rule, both in the free state as Graphite and combined with the Iron as Iron Carbide.

When cast Iron is dissolved in dilute Hydrochloric acid, the free Carbon is left undissolved as a black spongy precipitate, and the Hydrogen evolved has a very unpleasant smell, owing to the presence of various Hydrocarbons produced by the Carbide of Iron. Other impurities, such as Sulphuretted Hydrogen and Phosphine, are also evolved, owing to the presence of Sulphur and Phosphorus in the cast Iron.

When the Carbon present in cast Iron is mostly in the free state, it is called *grey pig iron*, and when it is mostly in the combined state, it forms *white pig iron*.

Cast Iron cannot be used for any articles which are liable to shocks, as it is brittle and has little tensile strength; also it cannot be welded like wrought Iron. It melts into a fairly mobile liquid, and can therefore be readily cast into any required shape.

Wrought Iron is a very pure form of the metal, which is obtained from cast Iron by getting rid of its impurities. This is brought about by heating cast Iron in a reverberatory furnace (p. 362), the bed of which is lined with pure powdered Haematite, Fe_2O_3 . The impurities are either oxidized by the Oxygen in the Haematite or form a slag with it. After a time the Iron becomes "pasty" because pure Iron has a higher melting point than impure Iron. It is stirred well through an opening in the side of the furnace, and finally gathered into large "balls" in somewhat the same way as butter in a churn. These "balls" are taken out of the furnace and squeezed under a steam hammer to get rid of the slag, and are then rolled into sheets or rails, which process gives the metal a fibrous structure.

Wrought Iron usually contains over 99 per cent. of the metal. It melts about 1500°C ., but begins to soften at 1000°C . and can then be welded.

It possesses great tensile strength, is very tough and malleable, and can be rolled into thin plates or drawn out into wire. It is used in the manufacture of articles too numerous to mention, but is not made so much use of nowadays as it used to be, its place being taken by mild Steel.

Wrought Iron differs from Steel in that, when made red hot and suddenly cooled, it does not harden as Steel does; also, when magnetized, it is capable of a much higher degree of magnetization than Steel, but it loses it all the moment the magnetizing force is removed, which Steel does not.

Steel is a mixture of Iron with from $\frac{1}{2}$ to $1\frac{1}{2}$ per cent. of combined Carbon; the greater the amount of Carbon, the harder is the Steel.

Steel is manufactured by several different processes, of which three will be considered here.

(1) *The Cementation Process.* In this process bars of pure wrought Iron are packed with Charcoal in firebrick boxes and heated in a furnace, to a temperature of about 1000°C ., for about 10 days. During this time the Carbon is slowly

diffusing into the Iron and combining with it, and the result is called *blister steel*, from its appearance.

When the heating is stopped after a shorter length of time, the surface of the Iron only is changed into Steel, and the process is termed *Case hardening*.

Crucible Steel is made in a similar way, but at a much higher temperature, by melting pure wrought Iron with Charcoal in a crucible. By this means the absorption of the Carbon is much quicker, and the process is finished in 4 hours. Crucible Steel is a very hard form of the metal, and is used for sharp-edged tools, such as razors, files, etc.

(2) *The Bessemer Process*. In 1856 Bessemer discovered that if a blast of air is forced through molten pig Iron, the impurities are all oxidized and removed by the blast, leaving very nearly pure and malleable wrought Iron.

The process is conducted in a *converter* (p. 401), which holds about 10 tons; molten pig Iron is run in and the air blast turned on; the combustion of the Carbon, Sulphur, etc., keeps the temperature high till it is all burnt away, and the appearance of the flame tells the operator when this point is reached. Then the proper amount of molten *Spiegeleisen*—Iron containing a little Manganese and a known amount of Carbon—to turn the whole mass into Steel is run in, the blast turned on to mix the contents, which are then turned out and the Steel cast in moulds. The process takes about half an hour. The inside of the converter is lined with Dolomite, which absorbs that part of the Silicon and Phosphorus which is not oxidized by the blast.

(3) *The Siemen's-Martin Process*. In this process, pig Iron is heated by producer gas in a furnace, the bed of which consists of pure Haematite with some Dolomite. The Haematite supplies the Oxygen to oxidize the impurities and the Dolomite absorbs the Silicon and Phosphorus as in the Bessemer process. When a suitable degree of purity is reached, Ferromanganese or *Spiegeleisen* is added, as in the Bessemer process. The bath of molten Steel is then tilted on rockers, and the metal run off and cast into moulds.

The comparative composition of cast Iron, wrought Iron

and Steel is shewn by the following table, where three typical examples are represented :

	Cast Iron.	Wrought Iron.	Steel.
Carbon - - -	3·81	·10	·65
Silicon - - -	1·68	·05	·07
Phosphorus - -	·70	·15	·03
Sulphur - - -	·60	·05	·02
Manganese - , -	·41	·07	·40
Iron - - - -	92·80	99·58	98·83
	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>

The properties of Steel depend entirely on its previous history as well as on the amount of Carbon it contains. When Steel is heated to a high temperature and then suddenly cooled, it becomes glass-hard and very brittle. This operation is called *hardening* steel. If now it is again heated to a high temperature and allowed to cool slowly, it becomes comparatively soft and ductile, and the process is called *annealing*.

By the process of *tempering*, Steel may be obtained in almost any degree of hardness or softness, of ductility, brittleness or elasticity. The process of tempering consists in heating the Steel up to known temperatures—from 200° C. upwards—and then cooling it by plunging it into baths of oil which are kept at known temperatures.

The temperature of the Steel during tempering is judged by the colour of the thin film of Oxide which forms on its surface, this colour being pale yellow, straw-coloured, brown, and finally blue as the temperature rises. The film of Oxide may be seen on various Steel articles, such as watch springs, etc., where it has not been cleaned off.

Properties of Iron. Pure Iron is a bright white metal, which polishes readily. Its density is about 7·8.

It is not acted upon by dry air, but in moist air, in the presence of Carbon Dioxide, it acquires a coating of *rust* (p. 19). This process of rusting starts slowly, but continues very rapidly when once a film of Oxide has been formed on the metal. Red-hot Iron will decompose steam with the evolution of Hydrogen, and finely divided Iron decomposes boiling water.

Hydrochloric acid dissolves the metal with the evolution of Hydrogen, forming Ferrous Chloride, and dilute Sulphuric acid also evolves Hydrogen with the formation of Ferrous Sulphate, but hot concentrated Sulphuric acid is reduced to Sulphur Dioxide by the nascent Hydrogen.

The behaviour of Nitric acid towards Iron is peculiar and interesting. A cold dilute Nitric acid forms Ferrous Nitrate and Ammonia, which promptly unites with the acid to form Ammonium Nitrate. A stronger acid forms Ferric Nitrate and Oxides of Nitrogen are evolved. With concentrated Nitric acid (Sp. Gr. 1.45) there is no apparent action, but the nature of the surface of the metal is changed. It will no longer precipitate Copper from Copper Sulphate solution or Lead from a solution of Lead Nitrate, nor is it now affected by dilute Nitric acid. This inert Iron is said to be in the *passive state*, and the cause of it is, probably, a thin film of Oxide formed on the surface of the metal. The passivity can be removed by scratching or strongly rubbing the surface of the metal.

COMPOUNDS OF IRON.

Iron forms three compounds with Oxygen :

Iron Monoxide, Ferrous Oxide,	-	-	-	FeO.
Iron Sesquioxide, Ferric Oxide,	-	-	-	Fe ₂ O ₃ .
Magnetic Oxide of Iron, Ferroso-ferric Oxide,				Fe ₃ O ₄ .

Ferrous Oxide FeO is formed as a black, crystalline magnetic substance when Carbon Dioxide is passed over hot finely-divided Iron. It is also obtained when Ferrous Oxalate is heated out of contact with air. On exposure to air it oxidizes at once to Ferric Oxide.

Ferrous Hydroxide Fe(OH)₂ is formed as a white precipitate when Ammonia is added to a Ferrous salt in the absence of air ; in the presence of air it has a green colour, and is rapidly oxidized to Ferric Oxide.

Ferric Oxide Fe₂O₃. When Ammonia is added to the solution of a Ferric salt, a fox-red precipitate of Ferric Hydroxide,

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$\text{Fe}(\text{OH})_3$, is formed, and this precipitate when dried and heated leaves a red amorphous powder, Ferric Oxide, Fe_2O_3 .

This Oxide is also found in lustrous black hexagonal crystals in the mineral known as *Specular Iron ore*, and these crystals form a red powder when ground in a mortar.

Powdered Ferric Oxide is used as a polishing powder—jeweller's rouge—and also as a pigment.

Ferric Oxide is a "weak" base, and, hence, solutions of Ferric salts all hydrolyse and are acid to litmus.

Ferroso-ferric Oxide Fe_3O_4 is found native as *Magnetite*. It is formed when Iron or any of its Oxides are heated in air or in Oxygen, and also when Iron is heated in a current of Steam or Carbon Dioxide.

In composition it is probably a compound of Ferrous and Ferric Oxides, partly by reason of it being isomorphous with the minerals of the Spinel group and partly because, when dissolved in acids, it yields a mixture of Ferrous and Ferric salts.

By dissolving the two Oxides (or Hydroxides) of Iron in acids, two series of salts are obtained, which are called respectively Ferrous (Fe^{++}) and Ferric (Fe^{+++}) salts.

FERROUS SALTS.

Ferrous Chloride FeCl_2 is formed when Hydrochloric acid gas is passed over heated Iron wire or when Iron filings are heated in a small quantity of Chlorine gas. In both cases it sublimes in white deliquescent crystals. From a solution of Iron in Hydrochloric acid, it may be obtained in pale green crystals $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

Ferrous Sulphate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, also known as *green vitriol* and *copperas*, is obtained by dissolving Iron in dilute Sulphuric acid.

It is isomorphous with the Sulphates of Zinc, Magnesium, Chromium, Cobalt and Nickel, which have a general formula $\text{RSO}_4 \cdot 7\text{H}_2\text{O}$.

It is formed on a large scale by the oxidation of Iron Pyrites by air and moisture; the liquid which drains away contains Iron Sulphates and Sulphuric acid and is converted

into Ferrous Sulphate by adding scrap Iron and crystallizing the solution.

Ferrous Sulphate is used for blue pigments, in the manufacture of ink and as a mordant.

Ferrous Sulphide FeS is made by dipping a white hot bar of Iron into molten Sulphur, the two elements unite, and, being readily fusible, the Ferrous Sulphide falls to the bottom, and is obtained, on cooling, as a grey metallic-looking mass. It is used mainly for the preparation of Sulphuretted Hydrogen.

FERRIC SALTS.

Ferric Chloride FeCl_3 is obtained when dry Chlorine gas is passed over red-hot Iron wire or filings. It can be sublimed in a dry tube or bottle, and forms dark red hexagonal crystals, which are very deliquescent. Its solution hydrolyses readily, and precipitates an insoluble Oxy-chloride on boiling.

Ferric Sulphate $\text{Fe}_2(\text{SO}_4)_3$ is formed as a brown solution when Ferrous Sulphate is treated with a mixture of Sulphuric and Nitric acids :



The brown solution leaves white anhydrous Ferric Sulphate when evaporated to dryness.

With Potassium Sulphate, Ferric Sulphate forms the better known Iron Alum, $\text{K}_2\text{Fe}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$, which crystallizes in rose-violet octohedra.

Iron Disulphide FeS_2 occurs very commonly in nature as the mineral Iron Pyrites or Marcasite. It is found in the form of brass-yellow cubes as *Pyrite*, and in rhombic crystals as *Marcasite*, and the latter often possesses a peculiar radiating structure.

When heated in a stream of air it forms Ferric Oxide and Sulphur Dioxide, and this latter gas is used in the manufacture of Sulphuric acid.

Detection of Iron. Iron compounds, whether in the Ferrous or Ferric condition, yield a grey magnetic powder when reduced on Charcoal, and also tinge a Borax bead green in the reducing flame and yellow in the oxidizing flame.

The following table shews the different behaviour of Ferrous and Ferric salts towards various reagents.

Reagents.	Ferrous Salts.	Ferric Salts.
Ammonia - -	Dingy green ppt.	Fox-red ppt.
Potassium Ferri- cyanide.	Dark blue ppt.	Brown coloration.
Potassium Ferro- cyanide.	Light blue ppt.	Dark-blue ppt.
Potassium Sulpho- cyanide.	<i>Nil.</i>	Blood-red coloration.

COBALT.

Symbol, Co. Atomic Weight, 59.0.

Occurrence. The two principal ores of Cobalt are *Smaltine*, CoAs_2 , and *Cobalt glance*, CoAsS , and in both of these the Cobalt is often partially replaced by Nickel.

Preparation. The metal Cobalt is not often prepared, but may be obtained by reducing any of its Oxides in a current of Hydrogen.

Properties. Cobalt is a hard white metal, malleable and ductile, and, unlike Iron, does not tarnish in air. It possesses feeble magnetic properties, which it retains at a red heat; the other magnetic metals, Iron and Nickel, lose this property when heated.

Cobalt decomposes steam, forming Cobalt Monoxide, CoO , and the action of acids upon it is similar to their action on Iron, but takes place more slowly.

COMPOUNDS OF COBALT.

Cobalt forms three compounds with Oxygen: the Monoxide, CoO , which is basic; the Sesquioxide, Co_2O_3 , which has only feeble basic properties; and Cobalto-cobaltic Oxide, Co_3O_4 . The two last-named Oxides evolve part of their Oxygen when heated, leaving the Monoxide, and so must be accounted Peroxides.

The salts of Cobalt are all derived from the Monoxide and are of little importance. Most of them are of a pink colour when crystalline or in solution, but become blue when anhydrous. They may be used for invisible ink, as the blue colour shews up when the paper is warmed, but, on cooling, the Cobalt salt absorbs moisture from the air and becomes invisible again.

Cobalt Nitrate is used in analysis, as it forms coloured compounds, on heating, with the Oxides of Aluminium, Zinc and Magnesium, and with Phosphates, enabling them to be distinguished from other white infusible residues.

Detection of Cobalt. Cobalt salts tinge a Borax bead blue in both Oxidizing and Reducing flames.

The soluble salts give a black precipitate of Cobalt Sulphide with Ammonium Sulphide, which precipitate differs from the similarly-coloured Nickel Sulphide in being insoluble in excess of the reagent; they also give a reddish-brown precipitate of $\text{Co}(\text{CN})_2$ with Potassium Cyanide, which dissolves in excess of the reagent.

NICKEL.

Symbol, Ni. Atomic Weight, 58.7.

Occurrence. The chief ores of Nickel are *Kupfernickel*, NiAs , *Nickel glance*, NiAsS and *Nickel Blende*, NiS . All these ores contain Cobalt as well.

Preparation. Very pure Nickel is obtained by Mond's process. The ore is first roasted to form Oxides of Nickel and the Oxide reduced to the metal by Carbon Monoxide at a temperature of 300°C . The temperature is lowered to 100°C . and extra pressure is turned on; Nickel Carbonyl, $\text{Ni}(\text{CO})_4$, a volatile compound, is formed, which, as it escapes, is heated to 200°C .; when it decomposes, Nickel is deposited, and the Carbon Monoxide which is evolved can be used again.

Properties. Nickel is a hard white lustrous metal, both malleable and ductile, and capable of a high polish. Its action towards air, steam and acids is precisely similar to that of Cobalt (*q.v.*).

Nickel is used principally for Nickel-plating other metals, because it does not readily tarnish in air. The electrolytic bath consists of a solution of the double Sulphate of Nickel and Ammonium.

German Silver, which is used for coinage and electric wires, contains 25 per cent. of Nickel, with Copper and Zinc in varying proportions. *Nickel Steel*, which is now largely used for armour-plates, as it is very hard and tough, contains about 20 per cent. of Nickel.

COMPOUNDS OF NICKEL.

Nickel forms three Oxides: the Monoxide, NiO , the Sesquioxide, Ni_2O_3 and Nickelo-nickelic Oxide, Ni_3O_4 . Of these only the Monoxide possesses basic properties, and from it the salts of Nickel are obtained. These salts are of comparatively small importance.

Detection of Nickel. Nickel salts give to a Borax bead a brownish-violet tinge in the oxidizing flame, and a grey colour in the reducing flame.

The soluble salts give a black precipitate of NiS with Ammonium Sulphide, which dissolves in excess of the reagent, forming a brown solution, also a pale green precipitate of Ni(OH)_2 with Caustic Soda and a greenish-yellow precipitate of Ni(CN)_2 with Potassium Cyanide, which dissolves in excess of the reagent.

PROBLEMS.

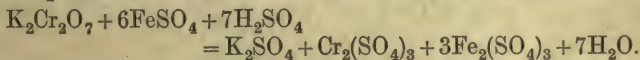
89. .5 gram of cast Iron was dissolved in Nitric acid. Ammonium Hydrate was added and the precipitated Ferric Hydrate was dried and changed into Ferric Oxide by heating. The weight of the Oxide was found to be .693 gram. Calculate the percentage of Iron in the specimen of cast Iron.

90. Find a formula for the compound having the following percentage composition:

Fe	-	-	14.28
N	-	-	7.14
H	-	-	5.12
S	-	-	16.32
O	-	-	57.14
			<hr/>
			100.00

PRACTICAL EXERCISES.

The Volumetric estimation of Metallic Iron. The estimation of Iron in solution depends for its working upon the oxidation of the Iron from the Ferrous state to the Ferric state. The usual oxidizing agents employed are Potassium Bichromate and Potassium Permanganate in the presence of Sulphuric acid. The equation, when Potassium Bichromate is used, is :



From this it is seen that 294 grams of Potassium Bichromate will oxidize 6 gram-atomic weights, *i.e.* $6 \times 56 = 336$ grams of Iron from the Ferrous state to the Ferric state.

The end of the reaction is marked by the disappearance of the last trace of Ferrous salt from the solution. This cannot be seen in the solution itself, nor is any reliable indicator available for use in the solution. Use is made of the very delicate reaction between Ferrous salts and Potassium Ferri-cyanide, the presence of 1 part in 1,000,000 of Ferrous Iron giving a blue tinge to this reagent.

Drops of the liquid which is being oxidized are taken out from time to time and tested with a drop of Potassium Ferri-cyanide, till no trace of blue is seen; this marks the entire change from Ferrous to Ferric Iron.

To prepare a standard solution of Potassium Bichromate. From the equation given above it is seen that 294 grams of Bichromate will oxidize 336 grams of Ferrous Iron to the Ferric state, so that 49 grams will oxidize 56 grams (*i.e.* the atomic weight in grams) of Iron.

A solution, therefore, containing 4.9 grams of Potassium Bichromate per litre is of such strength that 1 c.c. of it will oxidize .0056 gram of Iron.

To prepare it, melt 7 or 8 grams of pure Potassium Bichromate in a porcelain dish, allow to cool, break up the solidified salt, and weigh out accurately 4.9 grams of it. Dissolve this in a small quantity of distilled water in a beaker, transfer the solution and washings of the beaker into a litre flask and fill up to the mark with distilled water.

It is best next to confirm the oxidizing power of this solution by titrating it against a known weight of pure Ferrous Iron in solution.

To prepare a solution of Iron of known strength. Weigh out accurately 1 gram of pure Iron wire, place it in a flask, add 100 c.c. of dilute Sulphuric acid (1 to 8) and fit the flask with a bunsen valve.

This valve consists of a piece of thin rubber tubing about 3 in. long, fitted on to the short delivery-tube leading from the flask (which should have a rubber cork). The open end of the tube is closed with a piece of glass rod, and a slit about half an inch long is made with a sharp knife longitudinally in the rubber tubing: this allows gas or steam to escape from the flask, but, if the edges are cleanly cut, it will not permit air to come in from the outside, since the slit will be closed by the atmospheric pressure.

Thus no Oxygen from the air can get at the Ferrous solution while it is in a hot condition and very susceptible to oxidation; when cool it does not oxidize so easily.

While the Iron wire is dissolving, boil about 300 c.c. of distilled water in a flask to expel all dissolved Oxygen, and allow to cool.

When all the Iron is dissolved, and the contents of the flask quite cool, quickly transfer the whole of the contents to a 250 c.c. flask, rinse out the flask which held the Iron solution with the boiled distilled water, pour the rinsings into the 250 c.c. flask, and fill up to the mark. This solution is clearly one which contains .1 gram of Iron in every 25 c.c. *N.B.*—It will not keep more than 24 hours.

To standardize the Potassium Bichromate solution. First make up a few c.c. of a solution of Potassium Ferricyanide, and place a dozen or so drops of it on a white china plate; these drops serve as an indicator.

Then take 25 c.c. of the freshly prepared solution of Iron (which is in the Ferrous state) in a beaker, and add to it gradually the Bichromate solution from a burette. *Stir the mixture very thoroughly* with a light glass stirring-rod (made by closing up the ends of a piece of glass tube), take out one

drop on the end of the stirrer, and place it in one of the drops of Ferrieyanide on the white plate. If a blue colour is seen, it follows that there must be still some Iron present in a Ferrous condition—unoxidized.

Continue to add the Bichromate, stirring well after each addition, till no trace of the blue colour is seen in the indicator, and only a reddish coloration appears: this should be produced by the addition of only one drop of Bichromate solution, since the last trace of blue colour was seen.

Now note the volume of Bichromate added.

Since 25 c.c. of the Iron solution contain .1 gram of Iron, it follows that, if x c.c. of Bichromate solution have been added, 1 c.c. of this solution must be equivalent to $\frac{1}{10x}$ gram of Iron. $\frac{1}{10x}$ should be equal to .0056, if the solutions have been accurately prepared.

To find the percentage of Iron in Ferrous Sulphate crystals. Weigh out 4 grams of pure recrystallized Ferrous Sulphate, dissolve it in air-free distilled water, making the solution up to 100 c.c. Titrate 25 c.c. of this solution, to which a few c.c. of dilute Sulphuric acid have been added, against the standard Potassium Bichromate solution, as described above, and hence calculate the percentage of Iron in the salt.

When Iron is present in solution in the Ferric condition, its determination is performed by first reducing it to the Ferrous condition, and then titrating with standard Potassium Bichromate solution.

To determine the percentage of Iron in Iron Alum ($K_2Fe_2(SO_4)_4 \cdot 24H_2O$). Weigh out 10 grams of Iron Alum, and dissolve it in water; add a little Sulphuric acid, and make up the solution to 250 c.c.

The reduction of the Ferric Iron may be brought about by two methods:

(1) *Reduction by means of Zinc.* Take 100 c.c. of the Iron Alum solution in a flask fitted with a bunsen valve (see

above). Add 20 c.c. of strong HCl and about 5 grams of pure granulated Zinc, free from Iron.

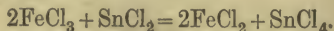
The nascent Hydrogen produced by the action of the acid on the Zinc will reduce the Ferric to Ferrous Iron.

When all the Zinc has dissolved (heat may be applied if necessary) and the solution cooled, it is transferred to a 250 c.c. flask, which is filled up to the mark with air-free water.

The quantity of Iron present in this solution, and hence in the original Iron Alum, can be readily determined by the titration of 50 c.c. of it with Potassium Bichromate.

This titration must be performed at once, as the liquid does not keep.

(2) *Reduction by means of Stannous Chloride solution.* 25 c.c. of the Iron Alum solution are taken in a beaker, 2 or 3 c.c. of strong HCl are added, and the liquid heated to boiling. Clear freshly made Stannous Chloride solution is then added, drop by drop, from a pipette till the yellow colour of the solution just disappears; this indicates that all the Iron has been reduced to the Ferrous state by the Stannous Chloride according to the equation:



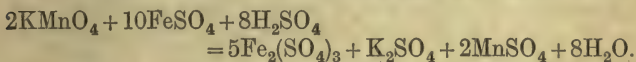
The excess of Stannous Chloride is got rid of by adding Mercuric Chloride solution, which *must* produce turbidity, shewing that excess of Stannous Chloride was present. The turbid liquid is then titrated with Potassium Bichromate solution, as described above, and the quantity of Iron in it ascertained; hence the percentage of Iron in Iron Alum can be readily calculated.

To determine the percentage of Iron in Haematite. Weigh out accurately 2 or 3 grams of powdered Haematite (or any similar ore of Iron). Digest the solid with about 20 c.c. of hot strong Hydrochloric acid in a beaker for five minutes. Pour off the solution into a 250 c.c. flask and add more Hydrochloric acid to the undissolved residue, continuing this process till no colour is produced in the acid, shewing that all the Iron has been dissolved out of the ore.

Fill up the 250 c.c. flask to the mark with distilled water, and estimate the quantity of Iron in the solution by reducing it to the Ferrous state and then titrating 25 c.c. of it with standard Potassium Bichromate solution.

Estimation of Iron by means of Potassium Permanganate. Owing to the fact that Potassium Permanganate oxidizes Ferrous Iron to the Ferric state in a similar manner to Potassium Bichromate, it may be used instead of the Bichromate for estimating the amount of Iron present in a solution.

The oxidation of Ferrous Sulphate is shewn in the equation :



From this equation it is seen that 316 grams of Potassium Permanganate will oxidize 10×56 , i.e. 560 grams of Iron from the Ferrous to the Ferric state.

A solution of 3.16 grams of the Permanganate in a litre of distilled water is therefore of such a strength that 1 c.c. of it is equivalent to .0056 gram of Iron.

In titrating the Iron solution with Permanganate, a little Sulphuric acid must first be added, and the liquid kept cool during the titration. The Permanganate acts as its own indicator, as described on page 461.

N.B.—Potassium Permanganate solution cannot be used for the oxidation of Ferrous salts when Hydrochloric acid is present; hence reduction of Ferric salts preceding oxidation by the Permanganate cannot be made with Stannous Chloride; Zinc and Sulphuric acid must be always used.

Solutions of Potassium Permanganate do not keep well even if protected from the light. An old solution should therefore be standardized before use.

This is quickly and conveniently performed by weighing out .7 gram of pure Ferrous Ammonium Sulphate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, dissolving it in air-free distilled water and titrating at once against the Permanganate solution.

The Ferrous Ammonium Sulphate can be obtained in a very pure condition, and as it contains precisely one-seventh of its weight of Iron, the quantity of Iron titrated is .1 gram.

CHAPTER XXXVI.

THE PLATINUM METALS.

CERTAIN alluvial sands found chiefly in the Ural and Caucasus Mountains, if washed in the same way as in the case of Auriferous sands, yield a series of heavy metals, of which Platinum is by far the best known.

They are usually divided into two groups, the *heavy* Platinum metals, consisting of *Platinum*, *Iridium* and *Osmium*, and the *light* Platinum metals *Ruthenium*, *Rhodium* and *Palladium*.

All these metals are silvery white and lustrous. They melt at a very high temperature, and are not acted upon by air or Oxygen at any temperature except in the case of Osmium, which forms its Tetroxide, OsO_4 .

Except Palladium, which dissolves in hot Nitric acid, none of the metals are affected by any single acid. *Aqua regia* attacks Osmium, forming the Tetroxide and it also dissolves Platinum, forming the Tetrachloride, PtCl_4 , but does not affect the other metals in the group.

All the metals shew great disinclination to form compounds, and such compounds, when formed, are easily reduced to the metal.

PLATINUM.

Symbol, Pt. Atomic Weight, 195.2.

History. Platinum has been known since the middle of the eighteenth century; it was brought from South America, and in 1788 the Spanish Government paid eight shillings a pound for it, probably to adulterate Gold. It was discovered in

the Ural Mountains in 1819, and is now practically a monopoly of the Russian Government. Its present price is more than £100 per lb.

Properties. Platinum is a grey-white metal with a brilliant lustre. It is harder than Gold or Silver, and is consequently more valued for the setting of jewellery. It is very ductile and malleable. It melts about 1750°C. , and as, like Iron, it softens before melting, it can be easily welded. Molten Platinum behaves like molten Silver, absorbing Oxygen and giving it out on solidification; hence it is liable to "spitting." It is of immense value to the chemist on account of its high melting point and the fact that it is not attacked by acids. Platinum crucibles and wire are used for very many chemical operations.

The fact that Platinum has the same coefficient of thermal expansion as Glass is made use of in chemical and physical apparatus; Platinum wires can be pushed through softened glass and make sound air-tight joints, which do not crack on heating or cooling. In this way it is used for making the connections in electric light bulbs.

Platinum Black is a black precipitate of metallic Platinum formed by the action of reducing agents upon solutions of Platinic Chloride, PtCl_4 ; *Spongy Platinum* is the metal left in a finely-divided spongy condition when the yellow precipitate formed by mixing Platinic Chloride and Ammonium Chloride (called Ammonium Chloroplatinate) is strongly heated; *Platinized Asbestos* is the finely-divided metal deposited on asbestos by dipping the latter into a solution of Platinic Chloride and heating to redness.

All these three forms of Platinum have very large surfaces of the metal for their weight, and possess the power of absorbing many times their volume of Oxygen, Hydrogen and other gases. They are of immense value as catalytic agents. Spongy Platinum will cause a mixture of Oxygen and Hydrogen to explode.

Its use in the manufacture of Sulphuric acid has already been noted. A jet of Hydrogen played on to Spongy Platinum makes the metal glow, and the jet is finally ignited. The

oxidation of wood-spirits to Formalin is brought about by this catalyst, as is the change of Alcohol to Acetic acid by union with the Oxygen in the air. Lately a process has been devised by which a mixture of Ammonia and air passed over Platinum black is changed into Nitric acid.

COMPOUNDS OF PLATINUM.

Platinum forms two compounds with Oxygen: Platinous Oxide, PtO , in which it exhibits di-valency and Platinic Oxide, PtO_2 , where it is tetra-valent. Two series of compounds, Platinous and Platinic, are derived from these Oxides, but they are of no great importance.

Detection of Platinum. All the salts of Platinum yield a grey deposit of the metal when ignited.

Solutions of Platinum salts give a yellow crystalline precipitate of $(\text{NH}_4)_2\text{PtCl}_6$ when Ammonium Chloride is added, and, if acidified with Hydrochloric acid, they yield a reddish-brown coloration containing PtCl_2 when Stannous Chloride is added to the liquid.

PROBLEM.

91. Assuming Potassium Platino-Chloride to have a formula K_2PtCl_6 , calculate the Atomic Weight of Platinum from the fact that 1.87 grams of the Platino-Chloride yield .75 gram of metallic Platinum when strongly ignited.

CHAPTER XXXVII.

RADIUM AND RADIOACTIVITY.

IN the year 1896 M. Henri Becquerel discovered that the metal Uranium and its salts were capable of affecting a photographic plate, even after being kept for a long time in the dark, and that they were constantly emitting rays comparable to some extent with those of light.

This property of Uranium salts may be shewn by wrapping an ordinary photographic dark slide, containing an unexposed plate, in black paper, placing a little Uranium salt on the top, and leaving the slide for some time in a closed drawer. When the plate is developed, it is found to have been affected as if by light, and a faint "image" of the heap of powder may be traced on it.

These same rays were also found to be capable of gradually discharging an electrified body placed in the neighbourhood of the Uranium salt.

In 1898 Madame Curie announced that she had obtained from *Pitchblende*, the ore of Uranium, a metal, to which she gave the name of *Polonium*, after Poland her native country, which possessed similar properties to Uranium, but to a much greater extent. Later, she announced the discovery in the same mineral of a still more active element, to which the name of *Radium* was given.

The method of extraction of the Radium (or its Chloride or Bromide) from *Pitchblende* is most intricate and needs the greatest care, which will be realized when it is stated that 1 ton of *Pitchblende* contains .37 gram of Radium.

The measurement of the radioactivity of a substance cannot well be made by using a photographic plate, but really accurate measurements have been obtained by using a special form of gold-leaf electroscope. This instrument (Fig. 154) is made of metal with glass sides and a loose bottom. It has only one gold leaf, which, when the instrument is un-

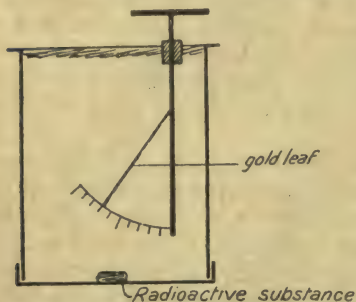


FIG. 154.—Electroscope for measuring Radioactivity.

charged, is at rest against a brass plate attached to the rod which communicates through an insulating rubber cork with the disc.

To work the instrument it is given a charge so that the gold leaf stands out from the brass plate as in the figure; the loose bottom is then taken out, the radioactive substance is placed upon it, and the bottom replaced. The

radioactivity of the substance is then judged by the length of time it takes to discharge the electroscope.

Gases may also be introduced into the instrument, and their radioactivity judged in the same way.

Radium is always found associated with Barium, and resembles it in most of its salts. The chemical reactions of the Chlorides of Barium and Radium are so similar that it is impossible to separate them, but a mixture of the Bromides can be separated to a very great extent.

Using Radium Bromide, the equivalent of Radium has been determined as 117.5 and, arguing from its analogy with Barium, it must have an atomic weight of 235, and has therefore one of the largest atomic weights of the elements.

Radium, like the alkaline earths, has a well-marked spectrum, the most prominent line being one in the blue part of the spectrum.

The rays emitted by Radium are very similar in their properties to the Uranium rays, but a million times more

intense. They cause phosphorescence in many substances, such as diamonds, rubies, the Sulphides of Zinc and Calcium, etc. A tube containing a grain or two of Radium Bromide, if kept near the human body, produces sores on the skin, which are most difficult to heal. It is, for this reason, usually carried in tubes made of Lead, which the rays do not penetrate very easily.

It has been announced that rays from Radium salts are a certain cure for many diseases, including cancer, and it is to be devoutly hoped that this announcement is not premature.

The rays emitted by Radium salts do not all possess the same properties, and have been divided by Madame Curie into three groups:

(1) The *Alpha rays* are only slightly bent when acted upon by an electromagnet; they have a positive charge and no great penetrative power. A sheet of Aluminium .0005 cm. thick reduces their intensity by one half. These are the rays which excite phosphorescence, as mentioned above, and which discharge electroscopes, etc. They are supposed to be material particles shot out from the Radium, possessing enormous energy and electric charges for their size.

(2) The *Beta rays* are very readily bent by magnetic influence, but in the opposite direction to the α -rays. They have a negative charge and great penetrative power, their intensity being halved by an Aluminium sheet .05 cm. thick. They are also believed to be material particles or "corpuscles," but of mass only $\frac{1}{1000}$ of the corpuscles of which the α -rays are composed.

(3) The *Gamma rays* are not affected even by most intense magnetic forces. They have enormous penetrative power, and will pass through several inches of Lead and several feet of Iron. These rays are believed to be a wave motion and not to be material particles.

M. and Mme. Curie discovered that any substance placed near Radium for some time acquired radioactive powers of its own, which gradually decrease when the Radium is removed, and finally disappear. This fact was discovered by Rutherford to be due to the continuous evolution of a substance from

Radium which behaved like a radioactive gas. This substance Rutherford called the Radium "*Emanation*." This emanation when kept by itself for a short time slowly decomposes, quite spontaneously, into a radioactive solid and Helium gas.

A similar degradation is also found to take place in the radioactive elements Uranium and Polonium, and in the latter case the products of the degradation are said to be Lead and Helium.

If these observations are correct, and there is little reason to doubt their accuracy, there is here a case, or cases, quite contrary to the fundamental idea of the immutability of the atom, for there is a genuine change from the Radium atom to atoms of some other element and Helium. This opens up a vast field for conjecture and experiment as to whether all the other substances now considered elements may not be breaking down, but at such a slow rate, that their degradation is not noticeable.

Prof. H. E. Armstrong has suggested that all the radioactive elements are compounds of Helium with other elements, but this hypothesis has received scant consideration, and the modern hypothesis of Rutherford and Soddy is based upon the assumption that every atom consists of small systems of *electrons*, whirling round one another, but keeping their position and numbers in most cases. But, in the case of the radioactive elements, these systems of electrons are of an unstable character and break down into two or more stable systems. The matter is too deep to be gone into further in a book of this nature, but the whole subject of radioactivity opens up a most fascinating field for investigation.

CHAPTER XXXVIII.

SPECTRUM ANALYSIS.

WHEN the rays emitted by a white-hot source of light, as, for example, a lime-light, are passed through a glass prism, they are found to be split up into a band of light according to

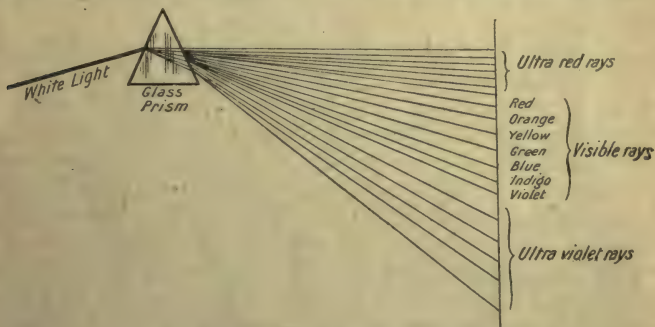


FIG. 155.—The Continuous Spectrum. (Diagrammatic.)

their refrangibility. The least refrangible rays are mainly those of Heat, and are called the *Ultra-red* rays. Next in point of refrangibility comes the visible part of the spectrum, the colour least bent being red, then orange, yellow, green, blue, violet and indigo. Still more bent than the visible rays are others called the *Ultra-violet* rays, whose presence is determined by their chemical action on a photographic plate.

The process of splitting up the original rays is shewn diagrammatically in Fig. 155.

It is a well-known fact that the salts of some metals, when inserted on a piece of Platinum wire in a bunsen flame, give various colours to the flame, *e.g.* Sodium salts colour the flame a vivid yellow, Copper salts green, Strontium salts crimson, etc. If these coloured flames are examined by means of a spectroscope, instead of the continuous band of colours produced by white light, the *spectrum* of each metal is found to consist of bright bands of light, varying in number, which occupy different parts of the coloured spectrum and are quite different and distinct for each element. A few of the spectra given by some of the elements are shewn in Fig. 156. Some of these may be a little misleading, for, as shewn in the diagram, Sodium has a *double* line in the yellow, Caesium a double line in the blue and Magnesium a double line in the green; these lines, when viewed through an ordinary spectroscope, appear as single lines, and their duplicity is only seen when the spectrum band is very much lengthened by refraction through more than one prism.

Mixtures of different metals give the lines characteristic of all the metals present, and the spectroscopic method forms a very valuable aid to the analyst.

It is also extremely delicate, and the presence of very minute quantities of an element is quite sufficient to give its spectrum; for instance, $\frac{1}{180,000,000}$ part of a grain of Sodium has been detected by the spectroscope and $\frac{1}{6,000,000}$ part of a grain of Lithium. This delicacy of perception is, in one way, rather a nuisance, as the minute quantities of Salt dust, which are always present in the atmosphere, are quite sufficient to produce the characteristic double yellow Sodium line in every spectrum.

Several metals have been discovered by the aid of spectrum analysis. The two alkali metals Rubidium and Caesium, whose salts are almost indistinguishable from those of the metal Potassium, were discovered by Bunsen in 1860, using the spectroscope, in some mineral waters. By its aid Crookes discovered the metal Thallium, which has a characteristic green line, from which it takes its name, and Indium and Gallium were also detected first by their spectra.

MAP OF SPECTRA
on a wave-length scale
showing the principal lines only.

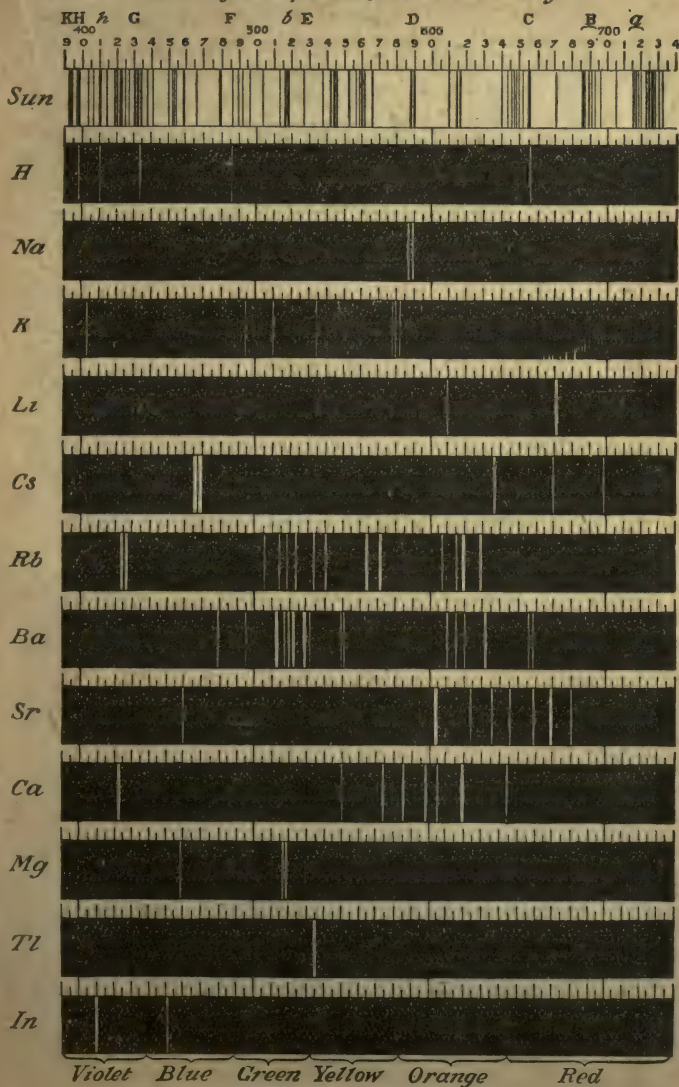


FIG. 156.—Spectra of Elements.

The spectrum of an element is an analysis of the colour evolved by the glowing vapour of the element, which must be in a state of vapour before it emits its characteristic colour.

Solids can usually be vaporized on a piece of Platinum wire held in the bunsen flame; if the temperature of this flame is not high enough for vaporization, they may be placed between the poles of an electric arc with its much higher temperature.

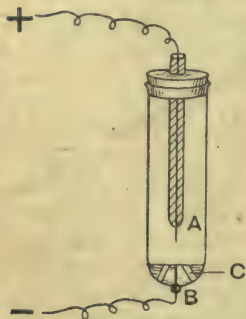


FIG. 157.—Tube for examining the spectra of liquids.

An arrangement for a spark spectrum, which is a very convenient one for liquids or minute quantities of solids, is due to Delachanel and Mermet, and is shewn in the diagram (Fig. 157). Sparks pass between the two Platinum terminals *A* and *B*, and a minute quantity of the liquid to be examined, *C*, is round the

lower terminal, and is vaporized by the heat of the discharge, and its spectrum examined in the usual way.

In Fig. 158 is shewn a tube, due to Crookes, used for the examination of the spectra of gases. The tube is filled with the gas to be examined, which is then partially exhausted



FIG. 158.—A Crookes' tube for examining the spectra of gases.

through the tube *A*, which is afterwards sealed up. The terminals of a Ruhmkorff's coil are joined up to the wires at the ends, and sparks pass rapidly through the rarefied gas, which glows brightly, especially in the narrow central part of the tube, where its spectrum can be readily examined.

The Solar Spectrum. In 1802 Wollaston noticed that in the spectrum produced by a beam of sunlight, the bright-coloured band was crossed by a large number of dark lines, and

these lines were very carefully mapped by Fraunhofer (1814), and are now usually called Fraunhofer's lines. A few of the more important of them are seen in Fig. 156.

It was soon noticed that the dark lines in the solar spectrum were coincident with the bright lines produced by the glowing vapours of known elements—for instance, in the diagram, it is seen that all the Hydrogen lines are reproduced in the solar spectrum—and the conclusion was drawn that these elements must be present in the sun.

The question might be asked, Why are the lines dark instead of bright? This question is answered in the following way. If the light from a bright arc is allowed to pass first through a bunsen flame in which a Sodium salt is held suspended by a Platinum wire, and then the light is analysed in a spectroscope, instead of the yellow Sodium line being intensified as might be expected, it is found to have disappeared altogether from the continuous spectrum, and a dark colourless "line" appears in its place. The reason given for this disappearance is that the glowing vapour of Sodium absorbs from the white beam of light the part of it which it emits itself.

A spectrum formed in this manner, of dark lines on a background of the continuous spectrum, is called an *absorption spectrum*.

In the sun there are developed all the conditions necessary to produce an absorption spectrum, the bright light of the white-hot interior having to pass through the glowing "atmosphere" before it reaches the earth and other planets. It is noteworthy that the light of the sun reflected from the various planets has a similar spectrum to that of the sun itself.

By comparing the sun's spectrum with that of single elements, the presence of no less than thirty-six elements has been determined in the sun's atmosphere or chromosphere, as it is usually called. The most abundant is Hydrogen, which is apparently present in vast quantities, and amongst other elements are Iron, Sodium, Calcium, Copper, Zinc, Manganese, Aluminium, Lead and Helium. The last-named element was

discovered in the sun by means of its spectrum, and derives its name from this fact ; it was not till much later that it was found to be present on the earth.

TABLE OF PRESSURES OF AQUEOUS VAPOUR
AT DIFFERENT TEMPERATURES.

Degrees Centigrade.	Pressure in mm. of Mercury.	Degrees Centigrade.	Pressure in mm. of Mercury.
5.0	6.5	13.0	11.2
5.5	6.8	13.5	11.5
6.0	7.0	14.0	11.9
6.5	7.2	14.5	12.3
7.0	7.5	15.0	12.7
7.5	7.8	15.5	13.1
8.0	8.0	16.0	13.5
8.5	8.3	16.5	14.0
9.0	8.6	17.0	14.4
9.5	8.9	17.5	14.9
10.0	9.2	18.0	15.4
10.5	9.5	18.5	15.8
11.0	9.8	19.0	16.3
11.5	10.1	19.5	16.9
12.0	10.5	20.0	17.4
12.5	10.8		

TABLE OF ATOMIC WEIGHTS.

Name of Element.	Symbol.	Approximate Atomic Weight.	International Atomic Weight, O = 16.
Aluminium - - -	Al	27	27.1
Antimony - - -	Sb	120	120.2
Argon - - - -	A	40	39.88
Arsenic - - - -	As	75	74.96
Barium - - - -	Ba	137	137.37
Beryllium - - -	Be	9	9.1
Bismuth - - - -	Bi	208	208.0
Boron - - - -	B	11	11.0
Bromine - - - -	Br	80	79.92
Cadmium - - - -	Cd	112	112.40
Caesium - - - -	Cs	133	132.81
Calcium - - - -	Ca	40	40.09
Carbon - - - -	C	12	12.00
Cerium - - - -	Ce	140	140.25
Chlorine - - - -	Cl	35.5	35.46
Chromium - - - -	Cr	52	52.0
Cobalt - - - -	Co	59	58.97
Copper - - - -	Cu	63.5	63.57
Erbium - - - -	Er	167.5	167.4
Fluorine - - - -	F	19	19.0
Gallium - - - -	Ga	70	69.9
Germanium - - -	Ge	72.5	72.5
Gold - - - -	Au	197	197.2
Helium - - - -	He	4	3.99
Hydrogen - - - -	H	1	1.008
Indium - - - -	In	115	114.8
Iodine - - - -	I	127	126.92
Iridium - - - -	Ir	193	193.1
Iron - - - -	Fe	56	55.85
Krypton - - - -	Kr	83	82.9
Lanthanum - - -	La	139	139.0
Lead - - - -	Pb	207	207.1
Lithium - - - -	Li	7	6.94
Magnesium - - -	Mg	24	24.32
Manganese - - -	Mn	55	54.93

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TABLE OF ATOMIC WEIGHTS (*Continued*).

Name of Element.	Symbol.	Approximate Atomic Weight.	International Atomic Weight, O = 16.
Mercury . . .	Hg	200	200.0
Molybdenum . . .	Mo	96	96.0
Neon	Ne	20	20.2
Nickel	Ni	59	58.68
Nitrogen	N	14	14.01
Osmium	Os	191	190.9
Oxygen	O	16	16
Palladium	Pd	107	106.7
Phosphorus	P	31	31.04
Platinum	Pt	195	195.2
Potassium	K	39	39.10
Radium	Ra	226.5	226.4
Rhodium	Rh	103	102.9
Rubidium	Rb	85	85.45
Ruthenium	Ru	101.5	101.7
Scandium	Sc	44	44.1
Selenium	Se	79	79.2
Silicon	Si	28	28.3
Silver	Ag	108	107.88
Sodium	Na	23	23.00
Strontium	Sr	87.5	87.63
Sulphur	S	32	32.07
Tantalum	Ta	181	181.0
Tellurium	Te	127.5	127.5
Thallium	Tl	204	204.0
Thorium	Th	232	232.0
Tin	Sn	119	119.0
Titanium	Ti	48	48.1
Tungsten	W	184	184.0
Uranium	U	238.5	238.5
Vanadium	V	51	51.06
Xenon	X	130	130.2
Yttrium	Y	89	89.0
Zinc	Zn	65	65.37
Zirconium	Zr	90.5	90.6

ANSWERS TO PROBLEMS.

1. $\left\{ \begin{array}{l} \text{N} = 86.17. \\ \text{O} = 11.90. \\ \text{CO}_2 = 1.93. \end{array} \right.$
2. 2.63 grams.
3. 1398 c.c.
4. 1.68 grams.
5. 10.1 grams.
6. 5.94 grams.
7. 7.21 grams.
8. 45.325 grams per litre.
9. 5.07 grams per litre.
10. 150 c.c.
11. (1) $\left\{ \begin{array}{l} 30.24 \text{ kilos Fe.} \\ 52.92 \text{ kilos H}_2\text{SO}_4. \end{array} \right.$
 (2) $\left\{ \begin{array}{l} 28.3 \text{ kilos Fe.} \\ 49.51 \text{ kilos H}_2\text{SO}_4. \end{array} \right.$
12. 60.17 kilos.
13. $\left\{ \begin{array}{l} 87.6 \text{ O.} \\ 12.4 \text{ H.} \end{array} \right.$
14. 31.25 per cent. O.
15. 7.
17. 32.43.
18. 11.53.
19. 9.05.
20. 22.9.
21. 3.
22. 29.7.
23. 31.6, 62.9.
24. 34.93.
25. 40 per cent. Mg.
26. 103.7.
27. 119.0.
28. 26.6.
29. 68.6.
30. 8.79, RCl_3 ; 26.37.
31. 11.
32. 10.35.
33. 37.09.
34. 124.6.
35. 60.37.
36. $\text{C}_2\text{H}_4\text{O}_2$.
37. 39.5.
38. 31.21.
39. $\left\{ \begin{array}{l} \text{Density } 35.6. \\ \text{Formula } \text{CO}_2. \end{array} \right.$
40. $\text{C}_2\text{H}_4\text{O}_2$.
41. 58,470 cal.
42. - 18,450 cal.
43. 88.8 per cent.
44. 1301 c.c.
45. .41 per cent.
46. 41.84 grams per litre.
47. 1.27 grams.
48. $\left\{ \begin{array}{l} 757.5 \text{ c.c.} \\ 815 \text{ c.c.} \end{array} \right.$
49. .252 gram.
50. .4176 gram.
51. .945 gram per litre.
52. .1597 gram per litre.
53. 7.476 grams.

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54. 25.73 per cent.
55. 1.29 grams.
56. $\begin{cases} .3825 \text{ gram.} \\ .765 \text{ gram.} \end{cases}$
57. 20.6 per cent.
58. 37.7 litres HCl.
59. 59.7 grams.
60. C_2H_6 .
61. C_4H_8 .
62. 6 c.c. CO + 12 c.c. H.
63. $\text{C}_4\text{H}_{10}\text{O}$.
64. $\text{CO}_2 : \text{H} : \text{O} :: 2 : 2 : 1$.
65. $\begin{cases} 37.5 \text{ c.c. O ; } 55 \text{ c.c. CO}_2 ; \\ 395 \text{ c.c. N ; some water.} \end{cases}$
66. 9.57 per cent.
67. 14.66.
68. $\begin{cases} 877 \text{ c.c. O.} \\ 292 \text{ c.c. CO}_2. \\ 585 \text{ c.c. SO}_2. \end{cases}$
70. $\begin{cases} 61.98 \text{ per cent. Pb.} \\ 38.02 \text{ per cent. Sn.} \end{cases}$
71. $\begin{cases} 103.45. \\ 206.9. \end{cases}$
72. 71.55 per cent.
73. $\begin{cases} .6288 \text{ NaCl.} \\ .3042 \text{ NaI.} \end{cases}$
74. 6.33 litres.
75. 63.04.
76. 65.2.
77. $\begin{cases} 51.95 \text{ per cent. CaCO}_3. \\ 48.05 \text{ per cent. SiO}_2. \end{cases}$
78. 56.2 per cent.
79. 102.08 grams per litre.
80. 32.5.
81. 95.4 per cent.
82. 99.65.
83. 84.9 per cent.
84. 10.
85. 27.27.
86. 52.02.
87. 6.69.
88. 2.275.
89. 97.02 per cent.
90. $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.
91. 194.82.

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K Na NH₃ all sol

NO₃ and acetates "

chlorides " except Ag Hgous Pb

Sulphates but Ba Sr Ca Pb

Carbonates

Phosphates } all insol K Na NH₃

Sulphates

Oxides

Hydroxides

Sulphides

K Na NH₃

Ba Sr Ca



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